



## **Regulation, formation, exposure, and treatment of disinfection by-products (DBPs) in swimming pool waters: A critical review**

**Yang, Linyan; Chen, Xueming; She, Qianhong; Cao, Guomin; Liu, Yongdi; Chang, Victor W.-C.; Tang, Chuyang Y.**

*Published in:*  
Environment International

*Link to article, DOI:*  
[10.1016/j.envint.2018.10.024](https://doi.org/10.1016/j.envint.2018.10.024)

*Publication date:*  
2018

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Yang, L., Chen, X., She, Q., Cao, G., Liu, Y., Chang, V. W.-C., & Tang, C. Y. (2018). Regulation, formation, exposure, and treatment of disinfection by-products (DBPs) in swimming pool waters: A critical review. *Environment International*, 15(10), 1039-1057. <https://doi.org/10.1016/j.envint.2018.10.024>

---

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



## Review article

## Regulation, formation, exposure, and treatment of disinfection by-products (DBPs) in swimming pool waters: A critical review



Linyan Yang<sup>a,b,c,d</sup>, Xueming Chen<sup>e</sup>, Qianhong She<sup>f</sup>, Guomin Cao<sup>a,d</sup>, Yongdi Liu<sup>a,d</sup>,  
Victor W.-C. Chang<sup>c,g,\*</sup>, Chuyang Y. Tang<sup>h,\*</sup>

<sup>a</sup> School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, PR China

<sup>b</sup> Interdisciplinary Graduate School, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

<sup>c</sup> Residues and Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, CleanTech One, Singapore 637141, Singapore

<sup>d</sup> Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, PR China

<sup>e</sup> Process and Systems Engineering Center (PROSYS), Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

<sup>f</sup> School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

<sup>g</sup> Department of Civil Engineering, Monash University, VIC 3800, Australia

<sup>h</sup> Department of Civil Engineering, University of Hong Kong, Pokfulam, Hong Kong

## ARTICLE INFO

Handling Editor: Robert Letcher

## Keywords:

Disinfectants

Disinfection by-products (DBP)

Precursors

Human exposure

DBP treatment

## ABSTRACT

The microbial safety of swimming pool waters (SPWs) becomes increasingly important with the popularity of swimming activities. Disinfection aiming at killing microbes in SPWs produces disinfection by-products (DBPs), which has attracted considerable public attentions due to their high frequency of occurrence, considerable concentrations and potent toxicity. We reviewed the latest research progress within the last four decades on the regulation, formation, exposure, and treatment of DBPs in the context of SPWs. This paper specifically discussed DBP regulations in different regions, formation mechanisms related with disinfectants, precursors and other various conditions, human exposure assessment reflected by biomarkers or epidemiological evidence, and the control and treatment of DBPs. Compared to drinking water with natural organic matter as the main organic precursor of DBPs, the additional human inputs (i.e., body fluids and personal care products) to SPWs make the water matrix more complicated and lead to the formation of more types and greater concentrations of DBPs. Dermal absorption and inhalation are two main exposure pathways for trihalomethanes while ingestion for haloacetic acids, reflected by DBP occurrence in human matrices including exhaled air, urine, blood, and plasma. Studies show that membrane filtration, advanced oxidation processes, biodegradation, thermal degradation, chemical reduction, and some hybrid processes are the potential DBP treatment technologies. The removal efficiency, possible mechanisms and future challenges of these DBP treatment methods are summarized in this review, which may facilitate their full-scale applications and provide potential directions for further research extension.

## 1. Introduction

Swimming is a popular activity for exercise and entertainment across the world. During pool activities, human substances (e.g., skin particles, sweat, urine, fecal, and hair) and personal care products (PCPs, e.g., sunscreen, body lotion, shampoos, and other cosmetics) can contaminate the swimming pool waters (SPWs). For outdoor pools, additional pollutants come from leaves and dust in the surrounding environment or from the rain water. These contaminants may carry pathogens, including bacteria, viruses and protozoa, which may result

in some diseases or symptoms such as gastroenteritis and dermatitis (Craun et al., 2005). Centres for Disease Control and Prevention (CDC) and Environmental Protection Agency (EPA) have conducted a 30-year surveillance program on waterborne outbreaks in the United States and the associated causes. During the monitoring period from 1971 to 2000, > 11,000 cases of illness and > 70 waterborne outbreaks were associated with swimming pools (Craun et al., 2005).

Disinfection plays a critical role in killing microbes and preventing the spreading of infectious diseases in SPWs. Nevertheless, disinfectants can react with water constituents of natural and anthropogenic origin to

\* Corresponding authors.

E-mail addresses: [victor.chang@monash.edu](mailto:victor.chang@monash.edu) (V.W.-C. Chang), [tange@hku.hk](mailto:tange@hku.hk) (C.Y. Tang).

<https://doi.org/10.1016/j.envint.2018.10.024>

Received 22 May 2018; Received in revised form 10 October 2018; Accepted 13 October 2018

Available online 02 November 2018

0160-4120/ © 2018 Published by Elsevier Ltd.

yield toxic disinfection by-products (DBPs) (Fischer et al., 2012). Researchers became aware of DBPs since early 1970 and > 600 DBPs have been reported in drinking waters (DWs) in the past 40 years (Richardson et al., 2007). Trihalomethanes (THMs) were the first identified DBP group with a concentration level of low to mid  $\mu\text{g/L}$  in DWs in 1974 (Rook, 1974), which have been linked with diseases such as bladder and colon cancer, asthma, irritation to the eyes and mucous membrane, and reproductive function (Aggazzotti et al., 2004; Erdinger et al., 1998; Goodman and Hays, 2008; Hamidin et al., 2008). Five years later, U.S. EPA constrained THMs with a maximum contaminant level (MCL) of 100  $\mu\text{g/L}$  in DWs (EPA, 1979). In 1998, the MCL of THMs was lowered to 80  $\mu\text{g/L}$  (EPA, 1998). At the same time, haloacetic acids (HAAs), another prevalent class of DBPs, were regulated with a MCL of 60  $\mu\text{g/L}$  for the sum of chloro-, bromo-, dichloro-, dibromo-, and trichloroacetic acids. THMs and HAAs account for nearly 25% of all halogenated DBPs (Krasner et al., 2006), of which chloroform, bromodichloromethane, dichloroacetic acid, and trichloroacetic acid have been classified as contaminants possibly carcinogenic to humans (Group 2B) by International Agency for Research on Cancer (IARC, 1999, 2004, 2014). Some emerging DBPs, though not yet regulated, can be potentially more toxic compared to THMs and HAAs, e.g., halonitromethanes (HNMs), haloamides, and iodo-DBPs (Richardson et al., 2007).

Public attention of DBPs in SPWs is not as much as that in DWs according to the number of publications in the past 20 years (Fig. 1). However, it is becoming an important topic due to the increasing popularity of swimming activities and its associated health side-effects. In addition to natural organic matter (NOM) from the source water, body fluids and PCPs released from the swimmers make the water matrix more complicated and possess a higher DBP formation potential. For example, urea, often found in SPWs at high concentrations, can react with free chlorine to form chloramine (Blatchley III and Cheng, 2010; Schmalz et al., 2011), which may lead to eye and upper respiratory tract irritation, biomarker changes in the lung, and development of asthma (Bernard et al., 2006; Massin et al., 1998).

The DBP concentrations in SPWs are often much or even several orders of magnitude higher than the MCLs in DWs or SPWs (Kanan et al., 2015; Parinet et al., 2012; Simard et al., 2013; Yang et al., 2016). The traditional SPW treatment train based on flocculation, sand filtration, and chlorination is inadequate to meet the current water quality standard. It is worth noting that DBP exposure during swimming can be much greater than that via DWs (Villanueva et al., 2006; Villanueva et al., 2007b), particularly for the more volatile compounds such as THMs. For example, only 1% of THM uptake during pregnancy was from DWs via oral ingestion, and 23% from swimming activities by inhalation and dermal absorption (Villanueva et al., 2007b). In view of

their critical importance, a comprehensive review is warranted to summarize the occurrence, formation and treatment of DBPs in the context of SPWs.

This review overviews the latest research progress of DBPs in SPWs from the following aspects: DBP regulations in different regions and by different organizations, formation mechanisms linked with different disinfectants, precursors and other various conditions, human exposure assessment reflected by biomarkers and epidemiological evidence, and the latest approaches for the control and treatment of DBPs.

## 2. Regulations and guidelines of DBPs

Regulations and guidelines have been established for DBPs in DWs, mainly covering THMs, HAAs, haloacetonitriles (HANs), bromate, chlorate and chlorite, *n*-nitrosodimethylamine (NDMA), cyanogen chloride and 2,4,6-trichlorophenol (Table 1). THMs were first regulated by U.S. EPA in 1979 with a MCL of 100  $\mu\text{g/L}$  in DWs (EPA, 1979). In 1998, the MCL of THMs was lowered to 80  $\mu\text{g/L}$  and meanwhile HAA<sub>5</sub> (the sum of chloro-, bromo-, dichloro-, dibromo-, trichloroacetic acids) were for first time regulated at 60  $\mu\text{g/L}$  (EPA, 1998). Apart from four THM and five HAA compounds regulated by U.S. EPA, the MCLs for bromate and chlorite are 10 and 1000  $\mu\text{g/L}$ , respectively. In contrast, the European Union only regulates THMs (< 100  $\mu\text{g/L}$ ) and bromate (< 10  $\mu\text{g/L}$ ) (Directive, 1998). The World Health Organization (WHO, 2008) provides guideline values for a comprehensive list of 15 individual DBPs in DWs. In addition to THMs and HAAs, the WHO guidelines also include NDMA (0.1  $\mu\text{g/L}$ ), cyanogen chloride (70  $\mu\text{g/L}$ ), 2,4,6-trichlorophenol (200  $\mu\text{g/L}$ ), bromate (10  $\mu\text{g/L}$ ), chlorate (700  $\mu\text{g/L}$ ), chlorite (700  $\mu\text{g/L}$ ) and two individual HANs, i.e., dibromoacetonitrile (70  $\mu\text{g/L}$ ) and dichloroacetonitrile (20  $\mu\text{g/L}$ ). The DW quality standard prescribed by Singapore is largely based on the WHO guideline (NEA, 2008). DBP guidelines for Australian and Canadian DW quality are shown in Table 1 as well.

Unlike the systematic regulation of DBPs in DWs, only THMs in SPWs have been regulated in some European countries (Table 2). Based on DIN 19643, the MCL of THMs (calculated as chloroform) in SPWs is 20  $\mu\text{g/L}$  in Germany (DIN, 2012). Switzerland has provided the MCL of THMs of 30  $\mu\text{g/L}$  and Denmark has promulgated the regulation of THMs in SPWs to be under 25 or 50  $\mu\text{g/L}$  depending on the pool types (Simard et al., 2013). The French Agency for Food, Environmental and Occupational Health & Safety (ANSES) has set a mandatory value for THMs of 100  $\mu\text{g/L}$  and a guide value of 20  $\mu\text{g/L}$  (ANSES, 2012). Some other developed countries, for example, Singapore, Canada and the United States, still do not have regulations for DBPs in SPWs in spite of the high popularity of swimming activity in these regions. Based on the existing available regulations and guidelines, the MCLs of DBPs in SPWs are often comparable or even lower than these in DWs. However, the DBP concentrations are generally much higher in SPWs than in DWs (Section 3.3.1), leading to concerns over their potential effect on health.

## 3. DBP formation mechanism

### 3.1. Disinfectants

#### 3.1.1. Disinfectants and their aqueous chemistry

Chlorination is the most commonly used disinfection approach for SPW treatment (Afifi and Blatchley III, 2015; Kogevinas et al., 2010; Weng and Blatchley III, 2011). Chlorine based disinfectants mainly include chlorine gas ( $\text{Cl}_2$ ), sodium hypochlorite ( $\text{NaClO}$ ) and calcium hypochlorite ( $\text{Ca}(\text{ClO})_2$ ) (WHO, 2006) (Table 3). The hydrolysis and/or dissociation of these disinfectants produce hypochlorous acid ( $\text{HClO}$ ) and hypochlorite ion ( $\text{ClO}^-$ ) as the active ingredients for disinfection (Eqs. (1)–(4)). The equilibrium between  $\text{HClO}$  and  $\text{ClO}^-$  is pH and temperature dependent.

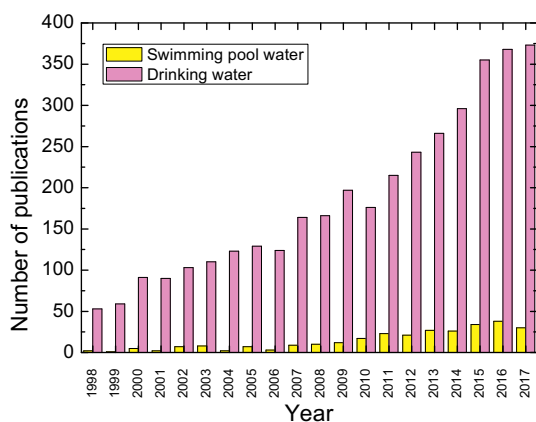


Fig. 1. The number of publications in relation with DBPs in SPWs and DWs in the past 20 years (1998–2017).

Source: Web of Science on Feb. 02, 2018. Keywords for searching: disinfection by-product, swimming pool water/drinking water.

**Table 1**  
DBP regulations and guidelines in drinking water.

DBPs	U.S. EPA (EPA, 1998)	WHO (WHO, 2008)	Singapore (NEA, 2008)	European Union (Directive, 1998)	Australia (NHMRC, 2011)	Canada (CDW, 2014)
MCL <sup>a</sup> (µg/L)						
THMs <sup>b</sup>	80	–	–	100	250	100
Chloroform	70	300	300	–	–	–
Bromodichloromethane	0	60	60	–	–	–
Chlorodibromomethane	60	100	100	–	–	–
Bromoform	0	100	100	–	–	–
HAA <sub>5</sub> <sup>c</sup>	60	–	–	–	–	80
Dichloroacetic acid	0	50	50	–	100	–
Trichloroacetic acid	20	200	200	–	100	–
Monochloroacetic acid	70	20	20	–	150	–
HANs	–	–	–	–	–	–
Dibromoacetonitrile	–	70	70	–	–	–
Dichloroacetonitrile	–	20	20	–	–	–
Others						
Bromate	10	10	10	10	20	10
Chlorate	–	700	700	–	–	1000
Chlorite	1000	700	700	–	800	1000
N-nitrosodimethylamine	–	0.1	–	–	0.1	0.04
Cyanogen chloride	–	70	70	–	80	–
2,4,6-Trichlorophenol <sup>d</sup>	–	200	200	–	20	5

Notes:

<sup>a</sup> MCL means maximum contaminant level.

<sup>b</sup> THMs refer to the summation of chloroform, bromodichloromethane, chlorodibromomethane, and bromoform.

<sup>c</sup> HAA<sub>5</sub> refer to the summation of chloro-, bromo-, dichloro-, dibromo-, and trichloroacetic acids.

<sup>d</sup> 2,4,6-Trichlorophenol has not been detected in swimming pool waters.



Bromine based disinfectants are used in pools under special conditions, e.g., spa. Liquid bromine, following the similar hydrolysis pattern of chlorine gas, is used for the maintenance of SPWs, especially for hot tubs (Eq. (5)). Some European countries have practiced using seawater as the source of SPWs since the early 1900s (Parinet et al., 2012). The bromide ion with a concentration of ~70 mg/L in seawater can be oxidized by HClO to form HBrO which plays a dominant role on disinfection (Eq. (6)) (Borges et al., 2005; Von Gunten and Oliveras, 1998). Parinet et al. (2012) pointed out that the formation of more toxic Br-DBPs (e.g., bromoform, dibromoacetic acid, and tribromoacetic acid) was substantial in seawater pools. Bromine with a lower vapour pressure overcomes the unstable property of chlorine under high temperature, such as spas and hot tubs (WHO, 2018). However, bromine based disinfectants are depleted rapidly under sunlight for outdoor pools and spas leading to the ill-suited applications (WHO, 2006).



**Table 2**  
DBP regulations and guidelines in SPWs.

Country	MCL <sup>a</sup> (µg/L)	Comments	References
Germany	20	THMs calculated as chloroform	(DIN, 2012)
Switzerland	30	THMs for indoor pools	(Simard et al., 2013)
Denmark	25 or 50	THMs (depending on the type of pools)	(Simard et al., 2013)
Belgium	100	Chloroform	(Simard et al., 2013)
France	100 or 20 <sup>b</sup>	THMs	(ANSES, 2012)
United Kingdom	100	THMs	(Simard et al., 2013)
Finland	100	THMs	(Simard et al., 2013)

Notes:

<sup>a</sup> MCL means maximum contaminant level.

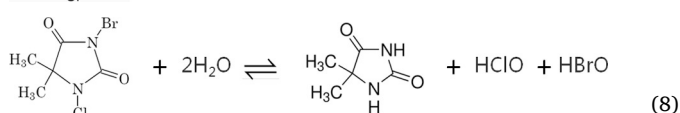
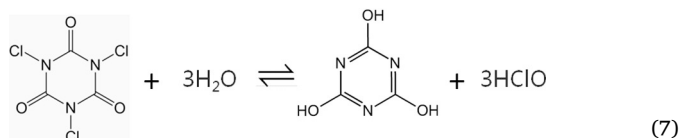
<sup>b</sup> The mandatory value for THMs is 100 µg/L and the guide value for THMs is 20 µg/L.

**Table 3**  
Disinfectant classifications.

Groups	Disinfectants
Chlorine based disinfectants	Chlorine gas Sodium hypochlorite Calcium hypochlorite
Bromine based disinfectants	Bromine liquid Sodium bromide + hypochlorite
Organic based disinfectants	Bromochlorodimethylhydantoin (BCDMH) Trichloroisocyanuric acid (TCCA) Dichloroisocyanuric acid (DCCA)
Others	UV Ozone Chlorine dioxide Hydrogen peroxide/silver/copper Combined disinfectants

Organic based disinfectants mainly include trichloroisocyanuric acid (TCCA), dichloroisocyanuric acid (DCCA), and bromochlorodimethylhydantoin (BCDMH) (Table 3). TCCA and DCCA are widely used in outdoor pools, especially for those exposed under strong sunlight, due to their role of chlorine stabilizer (Yang et al., 2016; Zwiener et al., 2007). The bound forms of chlorine in TCCA, i.e.,

monochloroisocyanurate ion ( $\text{HClCy}^-$ ) and dichloroisocyanurate ion ( $\text{Cl}_2\text{Cy}^-$ ), are more stable than  $\text{HClO}$  and  $\text{ClO}^-$  under the solar exposure, as the formers have much lower maximum absorption wavelengths (Wojtowicz, 1996, 2004). Askins (2013) has suggested that chlorine degradation slowed down with the presence of cyanuric acid under natural sunlight exposure. BCDMH is sometimes used for SPW disinfection (Lourencetti et al., 2012; Richardson et al., 2010). It shows better fecal coliform killing efficiency compared to commonly used  $\text{NaClO}$  (Moffa et al., 2006). However,  $\text{HBrO}$  as the highly reactive disinfection ingredient of BCDMH is unable to sustain the continuous disinfection requirement (Yang et al., 2016). The hydrolysis of TCCA (similar for DCCA) and BCDMH are shown in Eqs. (7) and (8), respectively.



Halogen-free disinfectants, e.g., UV and ozone, offer the advantages of minimizing the formation of halogenated DBPs. However, they are unable to sustain long time disinfection ability due to the lack of residuals. Chlorine dioxide produces chlorite and chlorate (Eq. (9)), which are mandatory regulated species in DWs (Table 1). Combined disinfections (e.g., UV + chlorine) are originally attempted to eliminate DBP formation. However this technology may only eliminate some DBPs (inorganic chloramines for instance) and enhance the formation of other DBPs (e.g., THMs, HANs, etc.) (Cheema et al., 2017; Cimetiere and De Laat, 2014; Weng et al., 2013) (see further discussion in Section 3.3.3).



### 3.1.2. Quantity control of disinfectants

Disinfection prevents some microbial-related infectious diseases spreading among swimmers in pools. The summation of  $\text{HClO}$  and  $\text{ClO}^-$  (active ingredients for disinfection) is defined as free chlorine (White, 1999). The quantity control of free chlorine in SPWs is essential. Its excess may cause discomfort to swimmers such as skin irritation and its insufficiency weakens microbial killing. Many countries have elaborated the free chlorine ranges in SPWs based on water conditions and/or pool types (Table 4). Singapore recommends a range of 1–3 mg/L for free chlorine (NEA, 2005). Based on Germany standard DIN 19643, the free chlorine ranges from 0.3 to 0.6 mg/L for swimming pools and from 0.7 to 1.0 mg/L for hot tubs (DIN, 2012). National Swimming Pool Foundation (NSPF) in the U.S. regulates free chlorine at 1–5 mg/L and recommends an ideal range of 2–4 mg/L (NSPF, 2006). Some states in the U.S. have their own free chlorine guidelines in pools, for example, 0.25–5.0, 1–10, and 1.5–5.0 mg/L in Colorado, Florida, and Georgia, respectively (CDPHE, 1998; DPH, 2013; FAC, 2009).

### 3.2. DBP precursors

DBP precursors in SPWs include NOM from the filling water (surface or ground water from water treatment plants), body fluids from the swimmers (e.g., urine, sweat, hair, saliva, etc.), and PCPs released from human skin or urine (e.g., sunscreen, body lotion, hand soaps, laundry detergents, shampoos, hair gels) (Chowdhury et al., 2014; Kim et al., 2002; Nassan et al., 2017; Zwiener et al., 2007). The additional body fluids and PCPs make SPW matrix more complicated and contribute to the higher potential formation of some conventional or emerging DBPs compared to DWs with NOM as the main organic source.

#### 3.2.1. Natural organic matter

NOM in SPWs mainly come from source or make-up water (normally DWs). Humic substances (i.e., humic and fulvic acids) account for the major fraction of NOM (52–70%) (Fan et al., 2001). Other hydrophilic substances (e.g., transphilic acids, proteins, amino acids and carbohydrates) account for 20–40%. NOM has been categorised as humic acids and hydrophobic/hydrophilic acid/base/neutral compounds by fractionation techniques (Matilainen and Sillanpää, 2010). NOM in DWs is in the range of 0.7–6.7 mg TOC/L and 0.1–0.3 mg TN/L in the U.S. (Kanan and Karanfil, 2011), 2.6–4.7 and 1.8–5.4 mg DOC/L in Norway and Australia (Fabris et al., 2008), and 1.1–1.4 mg TOC/L and 2.15 mg TN/L in Singapore (Yang et al., 2016). NOM has been proven to possess a high potential towards the formation of DBPs (e.g., THMs, HAAs, HANs, and HNMs) during chlorination (Kanan and Karanfil, 2011; WHO, 2008; Yang et al., 2016). The reduced TOC in treated SPWs or raw water corresponding to the substantially weakened formation potential of adsorbable organic halogens and THMs (AOX-FP, THM-FP) confirms that NOM acts as effective DBP precursors (Fabris et al., 2008; Glauner et al., 2005a, b). Fabris et al. (2008) reported an empirical relation between NOM and THM-FP as  $\sim 10\text{--}40 \mu\text{g THM-FP/mg DOC}$ . Therefore, it is an effective strategy to remove NOM via SPW treatment to reduce the DBP formation from the source.

#### 3.2.2. Body fluids

Human body fluids are released from swimmers during pool activities, where urine and sweat are two main sources of contaminants (Lamont Bradford, 2014). Judd and Black (2000) revealed that the actual pool condition is roughly approximated by 200 ml sweat and 50 ml urine per cubic meter of pool water. The release of urine and sweat into swimming pools has been estimated in a range of 25–77.5 and 200–1000 mL/bather, respectively (De Laat et al., 2011; WHO, 2006). Similar levels of urine and sweat release from swimmers have been reported in other literature studies, i.e., 54.7–117 and 823–1760 mL/bather by Weng and Blatchley III (2011), and 20–80 and 100–1000 mL/bather by Florentin et al. (2011). Sweat release is much higher than urine release especially during intensive exercises in pools operated with high temperatures. The sweat release rate is 0.04–0.91 L/m<sup>2</sup>/h as summarized by Keuten from previous publications and 0.1–0.8 L/m<sup>2</sup>/h as obtained from his own laboratory and on-site experiments (Keuten et al., 2014).

Urea is the main component in urine and sweat with a mean concentration of 10,240 and 680 mg/L, which accounts for 84% and 68% of TN, respectively (WHO, 2006). Urea in SPWs has been reported in many literature studies, e.g., 0.01–0.11 mg/L by Afifi and Blatchley III (2015), 0.50–2.12 mg/L by Schmalz et al. (2011), 0.12–3.6 mg/L by De Laat et al. (2011), 0.01–4.02 mg/L by Blatchley III and Cheng (2010). Our survey in Singapore pools shows a urea concentration of  $0.23 \pm 0.19 \text{ mg/L}$  (Yang et al., 2017b). Urea in an indoor pool increased by 72.4–155  $\mu\text{g/L}$  daily during a national swimming competition, which was equivalent to 0.56–1.20 g urea or 0.26–0.56 g TN released by each bather per day (Weng and Blatchley III, 2011). Similar urea release of 0.8–1.5 g/bather has been reported (WHO, 2006). The average release of pollutants during 30 min exercise is 250, 77.3, 37.1 and 10.1 mg/bather for non-purgeable organic carbon, TN, urea and ammonium, respectively (Keuten et al., 2014). Intensive usage of pools results in the substantial introduction of pollutants (e.g., urea, TOC, and TN), leading to adverse effects on water quality (Afifi and Blatchley III, 2015; De Laat et al., 2011; Weng and Blatchley III, 2011).

Apart from urea, creatinine (670–2150 mg/L), hippuric acid (50–1670 mg/L), citric acid (90–930 mg/L), ammonia (200–730 mg/L), uric acid (40–670 mg/L), glycine (90–450 mg/L), histidine (40–330 mg/L) present at substantial concentrations in urine can act as DBP precursors (Beach, 1971). A large portion of these nitrogenous compounds containing various functional groups ( $-\text{NH}_2$ ,  $-\text{COOH}$ ) and forms of bound nitrogen have been proven as efficient trichloramine precursors, particularly at acidic and neutral pH conditions (Afifi and



**Table 4**  
Regulated conditions for the operation of swimming pools.

Countries	Free chlorine	Combined chlorine (MCL <sup>a</sup> )	pH	References
US	<ul style="list-style-type: none"> <li>• Pools: 1–3 mg/L</li> <li>• Hot tubs, spa: 2–4 mg/L</li> <li>• Health care facilities: 15 mg/L (small hydrotherapy tanks, Hubbard tanks, tubs), 2–5 mg/L (whirlpools and whirlpool spa)</li> <li>• 1–5 mg/L (an ideal range of 2–4 mg/L in real operation)</li> </ul>		• 7.2–7.8	(Bottoni et al., 2014)
Canada (Quebec)	<ul style="list-style-type: none"> <li>• Indoor pools: 0.8–2 mg/L</li> <li>• Outdoor pools: 0.8–3 mg/L</li> <li>• Pools (T &gt; 35 °C): 2–3 mg/L</li> </ul>	<ul style="list-style-type: none"> <li>• Pools: 0.2 mg/L</li> <li>• Spa: 0.5 mg/L</li> <li>• Indoor pools: 0.5 mg/L</li> <li>• Outdoor pools: 1 mg/L</li> </ul>	• 7.4–7.6	(NSPF, 2006)
Germany	<ul style="list-style-type: none"> <li>• Pools: 0.3–0.6 mg/L</li> <li>• Spa (hot tubs): 0.7–1 mg/L</li> <li>• 0.4–1.5 mg/L</li> </ul>	• 0.2 mg/L	• 6.5–7.6	(DIN, 2012)
Spain			• 6.8–8.0	(Spain, 2007)
Australia (Queensland)	<ul style="list-style-type: none"> <li>• Indoor pools: &gt; 1.5 mg/L</li> <li>• Heated indoor pools (&gt; 26 °C): &gt; 2 mg/L</li> <li>• Outdoor pools: &gt; 1.5 mg/L</li> <li>• Heated outdoor pools (&gt; 26 °C): &gt; 3 mg/L</li> <li>• Spa (35–40 °C): &gt; 3 mg/L</li> </ul>	• 1 mg/L (not exceed half the total chlorine concentration)	• 7.2–7.8	(Queensland, 2004)
France	<ul style="list-style-type: none"> <li>• Pools (bleach or chlorine gas): 0.4–1.4 or 0.3–0.6 mg/L<sup>b</sup></li> <li>• Pools (isocyanuric acid derivatives): 2–4 mg/L</li> </ul>	• 0.6 mg/L	<ul style="list-style-type: none"> <li>• Pools: 6.9–7.7</li> <li>• Whirlpools: 6.9–8.2</li> </ul>	(ANSES, 2012, 2014)
London	• 1–2 mg/L			(WHO, 2006)
Italy	• 0.6–1.2 mg/L			(WHO, 2006)
Switzerland	<ul style="list-style-type: none"> <li>• Public and semi-public pools: &lt; 3 mg/L</li> <li>• Public and semi-public hot tubs: &lt; 5 mg/L</li> </ul>	• 0.2 mg/L	<ul style="list-style-type: none"> <li>• Chlorine disinfectants: 7.2–7.8</li> <li>• Bromine-based or other non-chlorine disinfectants: 7.2–8.0</li> <li>• 7.2–7.8</li> <li>• Artificial pools: 6.8–8.5</li> <li>• Natural pools: 6.0–9.0</li> </ul>	(WHO, 2006)
Singapore	• 1–3 mg/L			(NEA, 2005)
China	• 0.3–0.5 mg/L			(GB, 1996)

Notes:

<sup>a</sup> MCL means maximum contaminant level.

<sup>b</sup> The mandatory range of chlorine is 0.4–1.4 mg/L. The range can be 0.3–0.6 mg/L when the hygiene conditions of pools are met.

Blatchley III, 2015; Blatchley III and Cheng, 2010; De Laat et al., 2011; Lian et al., 2014; Schmalz et al., 2011). The release of nitrogenous compounds into swimming pools is between 320–840, 30–60, 15–50, 10–25 and 400–1000 mg/bather for urea, ammonia, amino-acids, creatinine and TN, respectively (Florentin et al., 2011).

In some lab-scale experiments, different recipes for body fluid analog (BFA) have been proposed to mimic swimmers' body excretions. A BFA recipe including urea (14,800 mg/L), creatinine (1800 mg/L), hippuric acid (1710 mg/L), histidine (1210 mg/L), citric acid (640 mg/L), uric acid (490 mg/L), ammonium chloride (2000 mg/L), and sodium phosphate (4300 mg/L) has been widely used for DBP formation potential tests in simulated pool conditions (Judd and Bullock, 2003; Kanan and Karanfil, 2011; Yang et al., 2016). This BFA represents a mixture of urine and sweat with a volume ratio of 1:4, in a concentration of ~5700 mg TOC/L and ~8700 mg TN/L. In the early stage, Judd and Black (2000) used a far more complicated BFA recipe with some additional inorganic compounds. Although this recipe is somewhat more representative of the real urine or sweat compositions (Beach, 1971), the additional inorganic constituents do not essentially affect the DBP formation. Kanan and Karanfil (2011) used three BFAs with different organic compositions to study their effect on DBP speciation. DBP formation potential tests of individual component showed that uric acid, citric acid, hippuric acid had significantly higher reactivity towards THM and/or HAA formation (Kanan and Karanfil, 2011; Yang et al., 2016), and that acid amides, particularly urea, ammonium ions and  $\alpha$ -amino acids were efficient trichloramine precursors (Schmalz et al., 2011).

The substantial DBP formation by human fluid raises public awareness of the importance of hygiene behaviour, i.e., have a shower before entering into the pools, do not urinate during swimming. However, a public survey among 1000 adults in the U.S. in 2009 showed that 35% of pool participants skipped the shower before

swimming and 17% had urination experience, and 84% believed their fellow swimmers engaged in unhygienic behaviours at public pools (Wiant, 2011). Keuten et al. (2014) found that 63% of pollutants in pools come from unhygienic behaviour at high exercise levels, of which 31% is caused by none pre-swim shower and 32% results from urination. The elimination of unhygienic behaviour has been shown to reduce the DBP formation by 55% in 35 °C and up to 68% in 25 °C, and these proportions are expected to increase at lower exercise levels (Keuten et al., 2014). A pre-swim shower of as short as 60 s can remove a significant amount of pollutants from human bodies (Keuten et al., 2012). It is essential to encourage or even enforce the swimmers to develop good hygiene habits.

### 3.2.3. Personal care products

Apart from the commonly discussed NOM and BFA, PCPs released by swimmers could be the potential precursors of chlorinated and oxidized or nitrogenous DBPs (Balmer et al., 2005). The more detectable PCPs in SPWs than in DWs are mainly attributed to the lower dilution ratio and high recirculation of SPWs. For example, the concentration of UV filters reached up to  $\mu\text{g/L}$  in SPWs or shower wastewater, which was several orders of magnitude higher than that in surface water (ng/L) (Bottoni et al., 2014; Lambropoulou et al., 2002).

Sunscreen is widely used in summer when pool activities are most popular. It aims at preventing skin damage under solar radiation via some commonly used active ingredients, e.g., 4-methylbenzylidene camphor (Serpone et al., 2002). Ekowati et al. (2016) provided a comprehensive review of 14 UV filters in swimming pools and spas and found that 4-methylbenzylidene camphor and 1H-benzotriazole had the highest concentration of 69.3 ng/L and the highest frequency of occurrence of 59%, respectively. Zwiener et al. (2007) have identified 5 active ingredients of sunscreens, namely 2-hydroxy-4-methoxybenzophenone, ethylhexyl methoxycinnamate,

**Table 5**  
THM concentrations in SPWs.

Country	THMs (µg/L)					Pool type <sup>a</sup>	References
	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	THMs		
U.S.	71 (25–207)	4 (1–28)	4 (1–10)	< 1	80 (26–213)	23 indoor (CI)	(Kanan et al., 2015)
	~25	< LOD	~2	< LOD		1 indoor (CI)	(Weng and Blatchley III, 2011)
	63 (16–138)		6 (1–35)	7 (1–55)	78 (19–146)	11 indoor (CI)	(Weaver et al., 2009)
	80–130					4 indoor (CI)	(Li and Blatchley, 2007)
	70–140					2 outdoor (CI)	(Li and Blatchley, 2007)
Canada	81 (12–282)		2 (N.D.–10)	1 (N.D.–32)	77 (33–282)	1 indoor (CI)	(Afifi and Blatchley III, 2015)
					44 (18–114)	15 indoor (CI)	(Simard et al., 2013)
					98 (12–311)	39 outdoor (CI)	(Simard et al., 2013)
	18–80					8 indoor (–)	(Lévesque et al., 2000)
	29 (13–46)				29 (13–46)	2 indoor (CI)	(Catto et al., 2012)
Germany					39 (5–125)	2 outdoor (TCCA)	(Zwiener et al., 2007)
					21	1 indoor (CI)	(Glauner et al., 2005b)
					35–47	2 outdoor (CI)	(Glauner et al., 2005b)
	18 (7–25)					1 indoor (CI)	(Erdinger et al., 2004)
	23 (21–27)	3 (2–3)	< 0.5	< 0.4	27 (25–30)	3 indoor (–)	(Cammann and Hübner, 1993)
Spain	3–28	0.7–6	0.03–7	0.02–0.8		Indoor (–)	(Cammann and Hübner, 1995)
					14 (6–43)	Indoor (–)	(Schmalz, 2012)
	15 (8–21)	14 (9–27)	13 (7–23)	7 (3–17)	50 (35–75)	1 indoor (CI)	(Richardson et al., 2010)
	< 0.3	< 0.7	2 (2–3)	57 (52–64)	60 (54–67)	1 indoor (BCDMH)	(Richardson et al., 2010)
	13.7 ± 7.3	1.4 ± 0.7	0.5 ± 0.5	0.3 ± 0.7	15.8 ± 7.2	20 indoor (–)	(Marina et al., 2009)
France					45.4 ± 7.3	1 indoor (CI)	(Kogevinas et al., 2010)
	15 (9–20)	14 (9–25)	13 (7–23)	7 (3–16)	50	1 indoor (CI)	(Lourencetti et al., 2012)
	< 0.3	< 0.6	2 (2–3)	60 (52–61)	63	1 indoor (BCDMH)	(Lourencetti et al., 2012)
	< 0.3	0.3 (0.1–1.1)	19 (3–64)	300 (29–931)	320 (32–996)	8 indoor (seawater)	(Parinet et al., 2012)
	67 (47–82)	9 (5–12)	3 (1–5)	1 (1–2)	80 (64–98)	3 indoor (CI)	(Villanueva et al., 2007b)
Australia	70	8	2	0.6	80	1 outdoor (CI)	(Manasfi et al., 2016)
	N.D.	N.D.	4 (2–5)	66 (49–87)	70 (50–92)	3 indoor (seawater)	(Manasfi et al., 2016)
	76 (65–84)	2 (2–3)	0.3–0.4	< 0.1	79 (67–87)	1 outdoor (CI)	(Yeh et al., 2014)
	33.2 ± 24.6	4.2 ± 1.3	1.9 ± 2.0	0.4 ± 0.5	39.8 ± 21.7	5 indoor (CI)	(Fantuzzi et al., 2001)
	88–116	17–18			105–133	3 indoor (CI)	(Stack et al., 2000)
England	121 (45–212)	8 (3–23)	3 (1–7)	1 (1–2)	132 (57–223)	8 indoor (CI)	(Chu and Nieuwenhuijsen, 2002)
Korea	21 (N.D.–46)	2 (N.D.–7)	N.D.	N.D.	23	86 indoor (three disinfectants)	(Lee et al., 2010)
Singapore	74 (30–167)	4 (1–12)	< 1	< 0.5	90 (32–170)	9 outdoor (–)	(Yang et al., 2016)

Notes: ND: not detectable; LOD: limit of detection.

<sup>a</sup> Chlorinated pools are indicated by CI in the brackets unless otherwise specified.

2-ethylhexyl-2-cyano-3,3-diphenyl-2-propenoate, 2-phenyl-1H-benzimidazole-5-sulfonic acid, and 4-methylbenzylidene camphor, with their total concentration ranging from single-digit to dozens of µg/L in outdoor pools. The higher bather load in the baby pool explains its higher sunscreen concentration than that in the adult pool. The 2-hydroxy-4-methoxybenzophenone produced considerably TOX (total organic halides) and THM after chlorination. The solar irradiation of a sunscreen agent, i.e., octyl-dimethyl-*p*-aminobenzoic acid, demonstrated its photolysis mainly via dealkylation and hydroxylation (Sakkas et al., 2003). In addition to the photo-transformation products of octyl-dimethyl-*p*-aminobenzoic acid detected in seawaters, the identification of some chlorinated intermediates in chlorinated SPWs demonstrates its potential role in DBP formation. Vidal et al. (2010) developed a method to identify six sunscreen ingredients (e.g., isoamyl 4-methoxycinnamate, 3-(4'-methylbenzylidene)camphor, 2-hydroxy-4-methoxybenzophenone, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, 2-ethylhexyl 4-dimethylaminobenzoate, and 2-ethylhexyl 4-methoxycinnamate). Only the former two species were detectable in a public swimming pool with concentrations of ~0.7 µg/L and < LOQ (limit of quantification), respectively. However, they were not detectable in a private pool, possibly due to the low bather load.

There are limited studies reporting the presence of sunscreen constituents in SPWs due to the high detection limit of current used analytical methods and lack of public concerns. Researchers started to conduct laboratory experiments to investigate their roles in DBP formation in the late 2000s. The halogenation of sunscreen regents relies on many parameters, e.g., chlorine concentration, solution pH, the presence of bromide ions, the compound structure, etc. (Nakajima et al., 2009; Negreira et al., 2008). Wang et al. (2013) conducted the

DBP formation potential tests for 4 body lotions and 4 sunscreens, and found the formation of an emerging DBP group, i.e., halobenzoquinones, such as 2,6-dichloro-1,4-benzoquinone with concentrations up to > 5000 ng/L and 2,6-dichloro-3-methyl-(1,4)benzoquinone with a concentration range of < 0.1–4.0 ng/L. Two orders higher of 2,6-dichloro-1,4-benzoquinone or other more detectable halobenzoquinone (e.g., 2,3,6-trichloro-(1,4)benzoquinone, 2,3-dibromo-5,6-dimethyl-(1,4)benzoquinone, and 2,6-dibromo-(1,4)benzoquinone) in SPWs than in tap water were attributed to the higher presence of these sunscreen precursors in SPWs. Nakajima et al. (2009) tested the chlorination of two sunscreen agents, i.e., octyl dimethyl-*p*-aminobenzoate and octyl-*p*-methoxycinnamate, in model swimming pool conditions and found the intensive appearance of some chlorine-substituted compounds. The mutagenicity of the chlorinated octyl-*p*-methoxycinnamate increased rapidly during the initial reaction stage and reduced to the control level later, indicating the formation of some unstable mutagenic intermediates. Negreira et al. (2008) identified the possible halogenated by-products of 2-ethylhexyl 4-(dimethylamino) benzoate, 2-ethylhexyl salicylate, and 2-hydroxy-4-methoxybenzophenone under chlorine exposure. The DBP formation was observed via aromatic substitution of hydrogen by halogen or cleavage of the carbonyl bond. The occurrence of five commonly used organic UV filters, including dioxibenzene, oxybenzone, avobenzone, 2-ethylhexyl-4-methoxycinnamate, and octocrylene, was reported in chlorinated seawater swimming pools with a total concentration of ~10 µg/L (Manasfi et al., 2015, 2017b). Bromoform and/or bromal hydrate (with higher cytotoxicity and genotoxicity than their chlorinated ones (Manasfi et al., 2017c; Plewa et al., 2008)) were identified as their transformation by-products due to the high presence of bromide in seawater, except

**Table 6**  
HAA concentrations in SPWs.

Country	HAAs (µg/L)										Pool type <sup>a</sup>	References
	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA	HAAs		
U.S.			700 (310–1330)	680 (370–1140)						1442 (800–2430)	6 outdoor (CI)	(Wang et al., 2014)
			727 (50–2040)	890 (20–2970)						1613 (70–3980)	6 indoor (CI)	(Wang et al., 2014)
			450 (50–750)	330 (40–530)						1067 (690–1360)	3 spa (CI)	(Wang et al., 2014)
Canada		2 (MRL-5)	777 (52–6787)	437 (76–1925)	21 (1–176)	8 (1–25)	34 (8–110)	6 (1–32)		1541 (172–9005)	23 indoor (CI)	(Kanan et al., 2015)
										364 (104–1195)	15 indoor (CI)	(Simard et al., 2013)
										808 (155–2224)	39 outdoor (CI)	(Simard et al., 2013)
										218 (111–390)	2 indoor (CI)	(Catto et al., 2012)
Germany			93 (48–192)	10 (54–191)	2 (1–3)		15 (< LOD–24)	< 0.5			3 indoor (–)	(Cammann and Hübner, 1993)
				206 (175–245)			1 (1–2)				Indoor (–)	(Stottmeister and Naglitsch, 1996)
	26 (3–81)	0.3 (< 0.5–3)	23 (2–192)	42 (4–199)		0.6 (0.2–8)					Hydrotherapy (–)	(Stottmeister and Naglitsch, 1996)
	32 (3–174)	0.2 (< 0.5–2)	9 (2–27)	15 (1–45)		0.6 (0.2–5)					Outdoor (–)	(Stottmeister and Naglitsch, 1996)
	26 (3–112)	0.1 (< 0.5–2)	132 (6–562)	249 (8–887)		0.1 (0.2–1)					Indoor (–)	(Schmalz, 2012)
Spain	2 (1–5)		19 (4–59)	10 (4–21)	2 (< 0.6–4)	< 1	5 (2–10)			39 (11–99)	Indoor (–)	(Cardador and Gallego, 2011)
	20 (9–36)		71 (60–91)	105 (85–125)						207 (154–251)	1 indoor (CI)	(Cardador and Gallego, 2011)
	26 (20–34)		154 (135–170)	122 (99–146)						302 (254–350)	1 outdoor (CI)	(Cardador and Gallego, 2011)
France	15–1000			1000–1700			208–912	< LOD–62	< LOD–15	1300–3200	3 (–)	(Loos and Barceló, 2001)
	4	N.D.	45	155	11	2	61	33	19	330	1 (–)	(Sarrion et al., 2000)
	15 (1–96)	42 (4–155)	4 (1–9)	22 (3–87)	50 (5–216)	234 (11–1089)	10 (1–20)	92 (36–243)	124 (4–428)	594 (84–2233)	8 indoor (seawater)	(Parinet et al., 2012)
	N.D.	N.D.	23	461	2	2	7	3	N.D.	498	1 outdoor (CI)	(Manasfi et al., 2016)
	N.D.	N.D.	N.D.	N.D.	4 (4–5)	66 (63–72)	N.D.	3 (3–4)	43 (36–53)	116 (109–132)	3 indoor (seawater)	(Manasfi et al., 2016)
Australia	59 (< 0.5–120)	< 0.5	1001 (230–2400)	1151 (110–2600)	< 0.5	< 0.5	12 (< 0.5–22)	< 0.5	–	2204 (366–5126)	7 outdoor + 5 indoor (CI)	(Yeh et al., 2014)
Korea			68 (14–246)	156 (20–636)							86 indoor (three disinfectants)	(Lee et al., 2010)
Singapore	22 (14–45)	< 2	370 (45–828)	437 (114–1020)	5 (1–9)	1 (0–1)	11 (5–19)	< 2	< 5	798 (191–1906)	9 outdoor (–)	(Yang et al., 2016)
China			81 (44–195)	52 (33–98)						156 (89–332)	5 outdoor (CI)	(Wang et al., 2014)
			34 (5–60)	53 (6–90)						95 (13–133)	9 indoor (CI)	(Wang et al., 2014)

Notes: ND: not detectable; LOD: limit of detection; MRL: minimum reporting levels. MCAA: chloroacetic acid; MBAA: bromoacetic acid; DCAA: dichloroacetic acid; BCAA: bromochloroacetic acid; TBAA: tribromoacetic acid; TCAA: trichloroacetic acid; BDCAA: bromodichloroacetic acid; DBCAA: dibromochloroacetic acid; DBAA: dibromoacetic acid.

<sup>a</sup> Chlorinated pools are indicated by CI in the brackets unless otherwise specified.



octocrylene as a chlorine resistant species.

Weng et al. (2014) found that only *N,N*-diethyl-*m*-toluamide, caffeine, and tri(2-chloroethyl)-phosphate were detectable in SPWs although totally 32 pharmaceuticals and personal care products (PPCPs) were tested. Teo et al. (2016) found the high occurrence of caffeine (up to 1540 ng/L) and ibuprofen (up to 83 ng/L) in chlorinated SPWs after a screen of 30 PPCPs. The absence of other PPCPs may be attributed to their chlorine-susceptible properties (transfer to DBPs by chlorination). Conversely, the accumulation of some PPCPs in SPWs may be caused by the slow reaction rate with chlorine, slow transfer from liquid to gas phases, or inefficient metabolism in humans. The insect repellent *N,N*-diethyltoluamide (DEET), commonly detected in swimming pool water samples, has been linked to the formation of nitrosamines during chloramination and chlorination (Shen and Andrews, 2011; Suppes et al., 2017). Parabens (known as hydroxybenzoate esters) are also widely used as preservatives in PCPs due to their broad antimicrobial spectrum and solubility in water (Alcudia-León et al., 2013; Terasaki and Makino, 2008). Terasaki and Makino (2008) for first time showed the appearance of parabens and its corresponding Cl-DBPs in SPWs. They found that benzylparaben as one of the parabens presents in SPWs at a concentration up to 28 ng/L (Terasaki and Makino, 2008). These authors also reported that a dichlorinated isopropylparaben was present in SPWs with a maximum concentration of 25 ng/L, and a dichlorinated methylparaben and a monochlorinated benzylparaben were detectable but lower than LOQs. Triclosan as an antibacterial agent, widely used in hand soaps, toothpastes, deodorants, mouthwash, etc., is a chlorine-sensitive compound. Its formation of chloroform and other Cl-DBPs under chlorination or chloramination has been reported (Greychock and Vikesland, 2006; Rule et al., 2005).

### 3.3. Factors affecting DBP formation

#### 3.3.1. DBPs in SPWs and DWs

Richardson et al. (2007) have summarized that a list of > 600 DBPs have been previously detected in DWs. However, a so-far comprehensive field survey conducted also by Richardson in Spain in 2010 showed > 100 DBPs in two large public swimming pools disinfected with NaClO or BCDMH. These DBPs included THMs, HAAs, HNMs, haloacids, halodiacids, haloaldehydes, halonitriles, halo ketones, haloamides, haloalcohols, and other halogenated and non-halogenated DBPs, many of which have yet been reported in SPWs and even do not exist in the current mass spectral library database (Richardson et al., 2010). Zwiener et al. (2007) has used GCMS to identify ~20 DBPs, including HAAs, other haloacids (e.g., 2,2-dichloropropanoic acid, 2-chloro-2-methylpropanoic acid, etc.), halo ketones (e.g., 1,3-dichloropropanone, etc.), and dichloromethyl methyl sulfone in two private outdoor swimming pools treated with stabilized chlorine in the U.S. In swimming pool treatment system, chlorination is the most widely applied or only designated disinfection approach. For example, France only permits the use of chlorine-based disinfectants (e.g., sodium hypochlorite, calcium hypochlorite or stabilized chlorine) in public pools since 2011 (Parinet et al., 2012). In Singapore, NEA authorizes chlorination as the sole disinfection method in SPW treatment. Other potential alternatives, e.g., ozone, chloramines, chlorine dioxide, commonly applied in DWs originally aiming at reducing Cl-DBP formation, may produce far more kinds of emerging non-chlorinated DBPs (Richardson et al., 2007; Sadiq and Rodriguez, 2004).

A large population-based survey ( $n = 500$ ) conducted in the U.S. reported the average THM and HAA concentrations of 38 and 23 µg/L respectively in DWs (Richardson et al., 2007). However, DBPs (HAAs in particular) in U.S. pools are far more than these values (see Tables 5 and 6). The higher DBP concentrations in SPWs than in DWs could be attributed to the following reasons: 1) the concentration of organic matter in SPWs (high-ppm levels, single- or even two-digit) is higher than that in DWs (low-ppm levels, single-digit or even less) (Kanan and Karanfil, 2011; Kanan et al., 2015; Wang et al., 2014); 2) there are more

organic species in SPWs (body fluids and PCPs in addition to NOM, see Section 3.2); 3) the recirculation of SPWs results in the accumulation of some stable and non-volatile DBPs, HAAs for instance (Kanan and Karanfil, 2011; Yang et al., 2016) (refer to Sections 5.2–5.4 for the DBP reactivity). A study shows that only about 1% of fresh water is added to the pools to offset the daily water consumption via evaporation and other losses, and therefore the retention time of SPWs reaches as high as 100 days (Arnaud, 2016).

#### 3.3.2. DBPs in different countries

DBPs in pools in different countries have been reviewed. A recent research article has summarized the occurrence of DBPs such as THMs, HAAs, HANs, haloacetaldehydes, haloamines, nitrosamines, and halo-benzoquinones in SPWs (Manasfi et al., 2017a). In the current paper, we aim to provide further insights towards the environmental occurrence of DBPs based on a more comprehensive review of THMs and HAAs (as a screen of other potential DBPs due to their abundant data availability) in SPWs. The THM concentrations in different countries listed in Table 5 are mostly in two-digit µg/L levels or occasionally slightly higher than 100 µg/L with one exception, i.e., 320 µg/L in a French study. The high THM concentration (CHBr<sub>3</sub> accounts for ~94%) in this study is mainly attributed to the use of bromide-rich seawater (68.1–106.7 mg/L as Br<sup>-</sup>) as the pool filling water (Parinet et al., 2012) (see more discussions in Section 3.3.4). In addition, CHBr<sub>3</sub> has higher molar mass and is less volatile than CHCl<sub>3</sub> (vapour pressure: 5.4 vs. 196 mm Hg), contributing to more severe contaminant accumulation.

The HAA concentrations in SPWs varied significantly in different countries (Table 6). For example, HAAs were in average only 39 µg/L in a German pool (Schmalz, 2012) and 95 or 156 µg/L in China pools (Wang et al., 2014). Nevertheless, several studies have reported the average HAA concentrations with > 1000 µg/L in the U.S. pools (Kanan et al., 2015; Wang et al., 2014) and 798 µg/L in Singapore pools (Yang et al., 2016). Moderate HAA concentrations were reported for most of Spain and France pools (~100–600 µg/L), with one exception that a Spain pool contains HAAs as high as 3200 µg/L (Loos and Barceló, 2001). The significant gaps between these values attribute in a large extent to the different ranges of disinfectant concentrations in pools regulated by different countries, for example, only 0.3–0.6 mg/L for German pools and 0.3–0.5 mg/L for China pools, but 1–5 mg/L for U.S. pools by NSPF and 1–3 mg/L for Singapore pools (Table 4). Fig. 2 illustrates that HAA concentrations increase significantly with the increasing chlorine in some countries where swimming activities are popular. In addition to chlorine regulation, other SPW characteristics (e.g., the loading and characteristics of organic inputs, the frequency of pool usage, and the hygiene habits of the bathers) and treatment conditions (e.g., filtration rate, water renewal rate, filtration media, etc.),

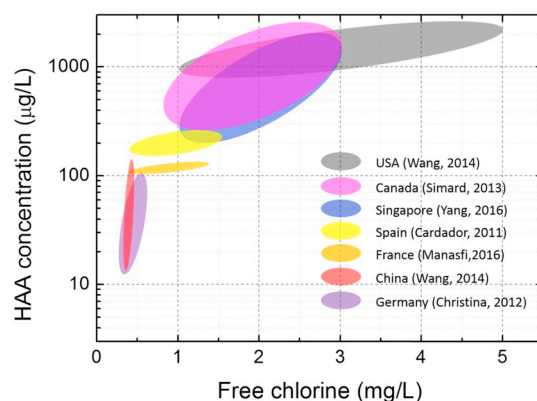


Fig. 2. The relationship between regulated ranges of free chlorine and HAA concentrations in SPWs in different countries. The coordinates of the ellipse vertexes represent the regulated chlorine ranges and reported HAA concentrations.

may contribute to the discrepancies of DBP concentrations as well.

### 3.3.3. DBPs formed by different disinfectants

Chlorination is the most commonly used disinfection technique for SPW treatment. Chloroform, di- and trichloroacetic acids are the main THM and HAA species for chlorinated pools, and bromoform, di- and tribromoacetic acids for brominated pools or chlorinated pools with bromide content (Tables 5 and 6). Bromoform accounted for only 14% for chlorinated pools with minor  $\text{Br}^-$  in source water and it increased up to 95% during bromination by BCDMH (Lourencetti et al., 2012; Richardson et al., 2010). Chlorinated isocyanurates (e.g., TCCA and DCCA) as stabilized forms of chlorine are easy for handling (manual input) and resistant to UV irradiation, therefore commonly used in private or outdoor pools exposed under sunlight (Bernard et al., 2008; Yang et al., 2016; Zwiener et al., 2007). The stabilized chlorine reduced chlorine consumption and DBP formation, mainly attributed to the more stable bound-chlorine species, i.e., monochloroisocyanurate ion ( $\text{HClCy}^-$ ) and dichloroisocyanurate ion ( $\text{Cl}_2\text{Cy}^-$ ) instead of  $\text{HClO}$  and  $\text{ClO}^-$  (Wojtowicz, 2004; Yang et al., 2016). A field study showed that DCCA reduced DBPs up to one order of magnitude compared to the common bleach (e.g., sodium hypochlorite, calcium hypochlorite) (Parinet et al., 2012).

Other disinfectants are also used in SPWs in some regions. In Korea, chlorine alone, the combined use of ozone and chlorine (ozone/chlorine), and a technique that uses electrochemically generated mixed oxidants (EGMOs), are three most commonly used disinfection methods. Ozone/chlorine seems to be the most chemical-safe method in terms of the formation of THMs, HAAs, HANs and chloral hydrate (Lee et al., 2009; Lee et al., 2010). The geometric mean concentrations of THMs in indoor SPWs were  $32.9 \pm 2.4$ ,  $23.3 \pm 2.2$ , and  $58.2 \pm 1.7 \mu\text{g/L}$  for chlorine ( $n = 72$ ), ozone/chlorine ( $n = 86$ ) and EGMO ( $n = 25$ ), respectively (Lee et al., 2009). Ozone as a partial substitute of chlorine reduced the total chlorine dosage therefore reduced the formation of Cl-DBPs. Nevertheless, ozone promoted the formation of some extra DBPs, e.g., bromate and nitrate, which are undesirable contaminants as well (Lee et al., 2010; Michalski and Mathews, 2007). A study in Poland showed that SPWs treated with chlorine dioxide generated more chlorite and chlorate compared to these with ozone (Michalski and Mathews, 2007). These DBPs have also been found in DWs treated with ozone or chlorine dioxide (Sadiq and Rodriguez, 2004). The summation of DBPs (including THMs, HAAs, HANs, and chloral hydrate) in chlorinated SPWs was significantly higher than that by combined chlorine and ozone based on an indoor pool survey (183 vs.  $33 \mu\text{g/L}$ ,  $n = 86$ ) (Lee et al., 2010). On the other hand, Richardson et al. (1999) reported that some emerging DBPs, e.g., 1,1-dichloropropanone and dichloroacetaldehyde, appeared at higher concentrations during the combined disinfection (chlorine + ozone) compared to chlorination only. The combined use of chlorine and UV had advantages of reducing genotoxicity compared to chlorination alone, which might be due to the less formation of Cl-DBPs (chloramine and HAAs for instance) (Cheema et al., 2017; Cimetiere and De Laat, 2014; Liviatic et al., 2010). However, UV irradiation promotes the formation of THMs and some nitrogenous DBPs (e.g.,  $\text{CH}_3\text{NCl}_2$ ,  $\text{CNCHCl}_2$ , and  $\text{CNCl}$ ) which might be more toxic than the carbon-based DBPs (Muellner et al., 2007; Weng et al., 2012; Weng et al., 2013). UV irradiation contributes to the simultaneous photolysis and UV-induced formation of NDMA, which is the most abundant toxic species of nitrosamines (i.e., as biomarkers of bladder cancer in humans (Walse and Mitch, 2008)), in the presence of chlorinated dimethylamine and monochloramine (Soltermann et al., 2013). Cassan et al. (2006) found the medium-pressure UV irradiation increased chloroform and bromodichloromethane via increased active chlorine or a progressive transformation of  $\text{CHBr}_3$ . Chloramination reduced the overall levels of some DBPs (e.g., THMs and HAAs) compared to chlorination but produced other DBPs, e.g., cyanogen chloride ( $\text{CNCl}$ ) and NDMA (Richardson et al., 2007; WHO, 2008).

### 3.3.4. Impact of filling water characteristics

In addition to the types and nature of disinfectants or organics (see Sections 3.1 and 3.2) in SPWs, the filling water characteristics including pH, temperature and the presence of bromide play significant roles in DBP formation as well. Proper pH adjustment in SPWs is necessary to ensure disinfection efficiency, secure user comfort and avoid pipe corrosion. The pH values have been regulated in different countries based on pool types or disinfectants (see Table 4). The pH range is 7.2–7.8 for pools in the U.S., Canada, Australia and Singapore, and wider ranges in Germany (6.5–7.6), Spain (6.8–8.0), and China (6.8–8.5 or 6.0–9.0). In general, lower pH is favoured as  $\text{HClO}$  is a more effective disinfection species than  $\text{ClO}^-$  (Sadiq and Rodriguez, 2004). Hansen and co-workers performed systematic investigations towards the pH effect on DBP formation (Hansen et al., 2012a, b, 2013). In general, with the decreasing pH within 6.0–8.0, THM formation decreased gradually, HAN and  $\text{NCl}_3$  formation increased, and HAA formation remained constant or decreased. Kanan (2010) similarly found that the formation of THMs and HAAs decreased by 40–60% with decreasing pHs from 8.0 to 6.0. The formation of THMs contains the alternate steps of hydrolysis and halogenation, which are favoured under high pH conditions (Bougard et al., 2008). HANs are expected to be increased due to their reduced hydrolysis under lower pH (Teo et al., 2015). The conflicting results for HAA formation may be attributed to the difference of organic sources in these experiments. The HAA formation was reduced by decreasing pH during the chlorination of filter particles from swimming pools (Hansen et al., 2012b). However, HAAs remained constant with the decreasing pH for BFA chlorination experiments (Hansen et al., 2012a). Acidic and neutral pHs are the most favourable conditions for  $\text{NCl}_3$  formation. Urea as one of the most effective  $\text{NCl}_3$  precursors has a relative  $\text{NCl}_3$  formation of 96% at pH 2.5 however only 24% at pH 7.7 (Schmalz et al., 2011). Low pH promotes  $\text{HClO}$  formation and therefore results in the protonation of bound nitrogen. In addition, low pH slows down  $\text{NCl}_3$  decay (Schmalz et al., 2011). Hansen et al. (2013) recommended a pH range of 6.8–7.5 for SPWs based on the calculated genotoxicity of DBPs (including THMs, HANs and  $\text{NCl}_3$ ). Overall, a comprehensive assessment based on disinfection efficiency, swimmer comfort, system stability and DBP formation is essential to establish the optimal pH range.

The temperature of SPWs influences the DBP formation as well. Simard et al. (2013) found higher concentrations of THMs, HAAs and inorganic chloramine in heated than non-heated outdoor pools (26 vs.  $23^\circ\text{C}$ ). An indoor swimming pool survey ( $n = 10$ ) in Canada illustrated higher halobenzoquinone formation at higher temperatures (Wang et al., 2013). Yang et al. (2016) also showed that THM concentrations almost or more than doubled when the temperature was increased from 25 to  $40^\circ\text{C}$ . However, the increase of HAAs was not as severe as that of THMs, which is possibly due to thermal decarboxylation of HAAs to the corresponding THMs (Lifongo et al., 2010). Kanan and Karanfil (2011) similarly found higher temperature contributed to higher THM than HAA yields. The DBP formation affected by temperature could be a combined result of several contributing factors, e.g.,  $\text{HClO}$  ionization, the kinetics of reactions between chlorine and organic matter, heat-promoted hydrolysis of bound chlorine/bromine if stabilized disinfectants are used, thermal stability of DBPs, etc. In addition, the sweat release rate increased from 0.1–0.2 to  $0.8 \text{ L/m}^2/\text{h}$  with the temperature increase from 29 to  $35^\circ\text{C}$ , which indicates that low temperature could restrain the continual anthropogenic pollutants released from the swimmers (Keuten et al., 2014).

The bromide present in the source water or as impurities in chemicals for SPW treatment plays a noticeable role in the formation of Br-DBPs. The SPWs are mainly supplied by DWs with a  $\text{Br}^-$  range of 36–2230  $\mu\text{g/L}$  based on a survey during 1997–1998 by U.S. EPA or with a small portion supplied by seawater with  $\sim 70$ –90  $\text{mg/L Br}^-$  (Kanan, 2010; Manasfi et al., 2016; Parinet et al., 2012). Bromoform, dibromoacetic acid, tribromoacetic acid, dibromoacetone, tribromonitromethane and bromonitromethane are the predominant

species of THMs, HAAs, HANs and HNMs in pools with the presence of bromide (Kanan, 2010; Manasfi et al., 2016; Parinet et al., 2012). The THM and HAA concentrations reached as high as 996 and 2233  $\mu\text{g/L}$  respectively (bromoform accounted for 93% of THMs, and dibromoacetic acid and tribromoacetic acid accounted for 70% of HAAs) in one of the eight chlorinated seawater pools (Parinet et al., 2012), which are far more than the average in chlorinated freshwater pools as shown in Tables 5 and 6. However, except THMs with comparable values, the concentrations of HANs, halo ketones, HAAs, trihaloacetaldehydes and HNMs in chlorinated freshwater pools were much higher than those in chlorinated seawater pools (Manasfi et al., 2016). This discrepancy may be related to other factors, e.g., the number of swimmers, solution pH and temperature, location of pools, physico-chemical properties of DBPs, etc. Nevertheless, the cytotoxicity and genotoxicity study based on 18 DBPs (including 6 HAAs, 6 haloacetamides, 3 HANs and 3 THMs) showed that Br-DBPs were substantially more toxic than their chlorinated analogs (Plewa et al., 2008). Hence, the use of seawater or freshwater with high bromide as pool filling water is undesirable with respect to Br-DBP elimination.

### 3.3.5. Impact of indoor and outdoor pools

The coverage of the pools, e.g., indoor or outdoor, has an impact on DBP formation as well. THM and HAA concentrations in outdoor pools were higher than those in indoor pools based on two studies (Cardador and Gallego, 2011; Simard et al., 2013). However, Li and Blatchley (2007) and Wang et al. (2014) found both indoor and outdoor pools in the U.S. had similar THM and HAA concentrations. The entries of additional precursors from the external environment (e.g., rain, dust, leaves) and the higher attendance rate in summer in outdoor pools may contribute to the higher DBP formation. Prolonged exposure of outdoor pools under solar radiation could also contribute to higher THM and HAA yields (Liu et al., 2006). However, the competing effects, such as solar photolysis of THM and HAA in outdoor pools (Chen et al., 2010), have a tendency to moderate their concentrations. The lower concentration of inorganic chloramines ( $\text{NCl}_3$  for instance) in outdoor pools was mainly caused by the solar UV photolysis and higher volatility of these compounds (Simard et al., 2013). Indoor environment may accumulate these volatile DBPs in the gaseous phases above the pool water levels if the ventilation are insufficient (Catto et al., 2012). Zwiener et al. (2007) pointed out that swimmers and even non-swimmers in indoor pools are exposed to a larger extent than in outdoor pools via inhalation of volatile DBPs (e.g., THMs and  $\text{NCl}_3$ ). Similarly, higher DCAA and TCAA were detected in workers' urine in indoor pools than outdoor pools although outdoor pools generally had higher HAAs (Cardador and Gallego, 2011). Therefore, the final DBP concentration in pools relies on the combined effects of formation, transformation and degradation.

## 4. Human exposure and risk assessment

### 4.1. Human exposure

Human bodies are exposed to DBPs mainly via three pathways: 1) inhalation of volatile compounds or aerosolized solutes; 2) dermal absorption by skin; 3) ingestion of DBP-contaminated water. In this section, we mainly reviewed the DBP exposure by assessing the corresponding DBP concentrations in bathers' or workers' body matrices including exhaled air, urine, blood, and plasma.

#### 4.1.1. THMs

Dermal absorption and inhalation are two main exposure routes of THMs (due to their percutaneous absorbable and volatile properties) during activities such as bathing, showering and swimming in indoor pools (Villanueva et al., 2007a, b; Xu et al., 2002). A level III fugacity model demonstrated the similar exposure level for dermal contact and inhalation for chloroform but higher for dermal contact for Br-THMs

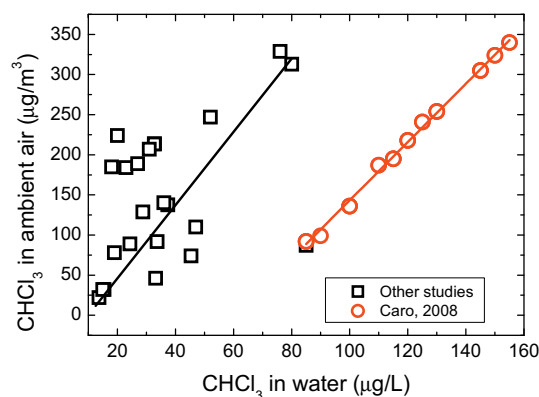


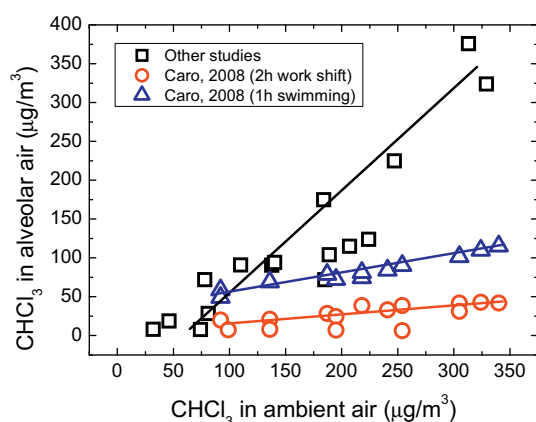
Fig. 3. The relationship between  $\text{CHCl}_3$  concentrations in swimming pool water and in ambient air. Other studies include (Catto et al., 2012; Fantuzzi et al., 2001, 2010; Kogevinas et al., 2010; Lévesque et al., 2000; Lourencetti et al., 2012; Marina et al., 2009; Richardson et al., 2010).

(Dyck et al., 2011). Erdinger et al. (2004) found that 2/3 of chloroform in the blood was taken up via inhalation and 1/3 via dermal absorption, assuming that accidental swallowing of water by divers is negligible. Similarly, Lourencetti et al. (2012) assessed the THM exposure by two predetermined actions, i.e., bathing in the water without exercise, and standing beside the pools. It showed dermal absorption (by subtracting the exposures in these two cases) accounted for ~40% of inhalation. The significant role of inhalation is mainly attributed to the high volatility of these compounds. For example, the vapour pressure of chloroform (196 mm Hg) is two orders of magnitude higher than that of trichloroacetic acid (1 mm Hg).

The crucial exposure of THM by inhalation attracts the public awareness of THM concentration in the ambient air especially in indoor environment with a relatively enclosed space. It is not surprising to observe a positive correlation between chloroform concentrations in SPWs and its corresponding ambient air as shown in Fig. 3 (Catto et al., 2012; Fantuzzi et al., 2001, 2010; Kogevinas et al., 2010; Lévesque et al., 2000; Lourencetti et al., 2012; Marina et al., 2009; Richardson et al., 2010). The chloroform concentrations obtained from an indoor public pool in Spain demonstrated an excellent linear correlation (Caro and Gallego, 2008). Bromoform as an abundant THM species in brominated and chlorinated bromide-rich SPWs, demonstrated its positive correlation between water and air phases as well (Boudenne et al., 2017; Manasfi et al., 2017a). The prediction of air concentration based on aqueous samples may be possible to avoid the complicated air sampling procedures. It should be noted that air concentrations are location-dependent. Higher THM concentrations were observed at lower levels above the water surface (Nitter et al., 2018). The average THM concentration in air in poolside ( $58.0 \mu\text{g}/\text{m}^3$ ) was more than double of that in the reception area and engine room ( $26.1$  and  $25.6 \mu\text{g}/\text{m}^3$ ) (Fantuzzi et al., 2001). Aprea et al. (2010) similarly found that the THM concentration in air near the pool was higher than those in places far away (e.g., change rooms, passageways and offices).

The THM concentrations in alveolar air of swimmers or workers could be a good indicator to evaluate human exposure. The  $\text{CHCl}_3$  in swimmers' alveolar air had a quite wide concentration range of  $\sim 10$ – $350 \mu\text{g}/\text{m}^3$  (shown as black squares in Fig. 4) (Catto et al., 2012; Fantuzzi et al., 2001, 2010; Kogevinas et al., 2010; Lévesque et al., 2000; Lourencetti et al., 2012; Marina et al., 2009; Richardson et al., 2010). Caro and Gallego (2008) have systematically investigated the THM exposure by human groups with different activities. The alveolar  $\text{CHCl}_3$  concentration increased 20 times for swimmers after 1 h swimming and only 8 times for workers after 2 h work shift. Similarly, Fantuzzi et al. (2001) found that the alveolar  $\text{CHCl}_3$  concentrations of pool trainers were almost doubled compared to those worked as reception participants and engine room technicians ( $25.1$  vs.  $14.8 \mu\text{g}/\text{m}^3$ ).

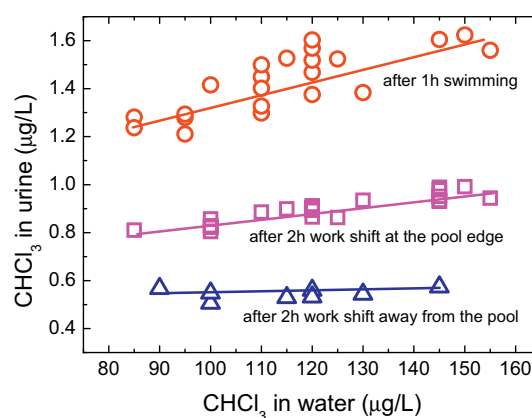




**Fig. 4.** The relationship between  $\text{CHCl}_3$  concentrations in ambient air and alveolar air of swimmers. Other studies include (Catto et al., 2012; Fantuzzi et al., 2001, 2010; Kogevinas et al., 2010; Lévesque et al., 2000; Lourencetti et al., 2012; Marina et al., 2009; Richardson et al., 2010).

The THM concentrations in alveolar air were highest for swimmers followed by those bathing in the pools without exercise and were lowest for those standing beside the pools (Lourencetti et al., 2012). It is worth noting that  $\text{CHCl}_3$  concentration in breathing zones of swimmers (i.e., boundary layer) was around 40 times higher than that in the ambient indoor air, which indicates that inhalation of  $\text{CHCl}_3$  by swimmers is more substantial than other non-swimmers (Chen et al., 2011). A good linear correlation between the  $\text{CHCl}_3$  concentrations in alveolar and ambient air further demonstrates the significance of inhalation for human exposure (Fig. 4). A strong correlation between the total THM levels in ambient air and exhaled breath of pool attendants have been reported as well (Fantuzzi et al., 2001). The  $\text{CHCl}_3$  concentration in the alveolar air reached up to  $124 \mu\text{g}/\text{m}^3$  after 1 h leisure activity, however  $376 \mu\text{g}/\text{m}^3$  for competition swimmers (Lévesque et al., 2000). Lourencetti et al. (2012) found that physical activity enhanced THM exposure by comparing swimmers with swimming activities and volunteers with bathing only. Intensive exercises speed up swimmers' breathing and THM mass transfer, and therefore enhance THM exposure via inhalation. In brominated pools,  $\text{CHBr}_3$  in swimmers' alveolar air reached up to  $\sim 10 \mu\text{g}/\text{m}^3$  and showed a correlation with its corresponding ambient air concentrations as well (Lourencetti et al., 2012). Overall, human exposure reflected by alveolar air mainly attributes to the THM concentration in ambient air and water, exposure time and human activities.

Urine is another matrix for human exposure evaluation. Aprea et al. (2010) found the  $\text{CHCl}_3$  concentration in urine increased from 0.123 to  $0.404 \mu\text{g}/\text{L}$  after some water activities. Caro and Gallego (2007) found the  $\text{CHCl}_3$  and  $\text{CHBrCl}_2$  concentrations in human urine were around 0.5 and  $0.02 \mu\text{g}/\text{L}$  respectively before any exposure in swimming pool environment. The concentrations increased 3 times after 1 h swimming and only 2 times after 2 h work shift. Even after 4 h work shift, the concentration cannot reach as high as that after swimming (Caro and Gallego, 2007, 2008; Caro et al., 2007). Both swimmers and workers suffer from THM exposure via inhalation, however, swimmers with more strenuous exercises than workers inhale more air with higher THM concentration (just above the water level). In addition, swimmers exposed directly in SPWs experienced two additional exposure routes, i.e., dermal absorption and ingestion. Fig. 5 shows that the staffs working near the pool (e.g., monitors and pool guardians) experienced much higher  $\text{CHCl}_3$  exposure than those working far away (e.g., receptionists and maintenance technician), which indicates the importance of the relative position to THM exposure. Fig. 5 also shows a good linear relationship between  $\text{CHCl}_3$  concentrations in SPWs and urine.



**Fig. 5.** The relationship between  $\text{CHCl}_3$  concentrations in swimming pool water and in the urine of swimmers after 1 h swimming and workers after 2 h work shift.

Data are from (Caro and Gallego, 2007, 2008).

#### 4.1.2. HAAs

The more polar HAAs are less volatile and permeable to skin, and therefore have a higher potential of exposure by ingestion (Xu et al., 2002). HAA concentrations in SPWs (Table 6) are generally much higher than those reported in DWs (Richardson et al., 2007), thus even a small amount of SPW ingestion may result in a substantial intake. Cardador and Gallego (2010) developed a sensitive and straightforward method (headspace gas chromatography - mass spectrometry, HS-GCMS) to detect HAAs in human urine with detection limits as low as  $\text{ng}/\text{L}$ , which established a technique foundation for the further investigation of HAA exposure among humans. Later these authors tested the urinary HAA concentrations of three groups of subjects to distinguish the respective role of three exposure pathways (Cardador and Gallego, 2011). They found that ingestion ( $\sim 94\%$ ) outcompeted inhalation ( $\sim 5\%$ ) and dermal absorption ( $\sim 1\%$ ) and became a major exposure route. The finding that the urinary HAA concentration of the testers after 1 h swimming was more than an order of magnitude higher than that after 2 h work shift further validates ingestion as a more decisive exposure route than inhalation (Cardador and Gallego, 2011). More specifically, TCAA, DCAA and MCAA were present in swimmers' urine with concentrations of  $\sim 4.4$ ,  $\sim 2.3$ , and  $\sim 0.56 \mu\text{g}/\text{L}$  respectively after 1 h swimming in indoor pools. Font-Ribera et al. (2016) similarly reported the urinary TCAA increased from 3.9 to  $12.3 \mu\text{g}/\text{L}$  after 40 min swimming in a chlorinated indoor pool. Urinary TCAA seems a better biomarker for ingestion exposure evaluation due to its longer biological half-life than other HAAs (Bader et al., 2004; Kim et al., 1999).

HAAs regardless of the low volatility were still detectable in air phase with a concentration range of  $5\text{--}64 \mu\text{g}/\text{m}^3$ , owing to a great amount of aerosols (reflected by the humidity) in some indoor swimming pools (Pereira et al., 2012). Workers around the pools without touching SPWs still can be exposed via inhalation of HAA-contaminated aerosols. Cardador and Gallego (2011) reported that DCAA and TCAA reached  $\sim 300$  and  $\sim 120 \text{ ng}/\text{L}$  in the urine of workers after 2 h work shift in indoor swimming pools. These values were several times higher than those reported in outdoor pools and the exposure increased with time (2 h vs. 4 h as shown in Fig. 6A, B). It indicates that sufficient ventilation in indoor pools is of high importance to ensure workers' safety. The linear relationship between HAA concentrations in human urine and SPWs as shown in Fig. 6 offers the possibility to estimate the human HAA exposure by known HAA concentration in SPWs (Cardador and Gallego, 2011; Cardador and Gallego, 2010). Hence, HAA exposure by pool participants varied with a number of factors, e.g., HAA concentrations in SPWs, pool types (indoor or outdoor), exposure time, human activities, etc.

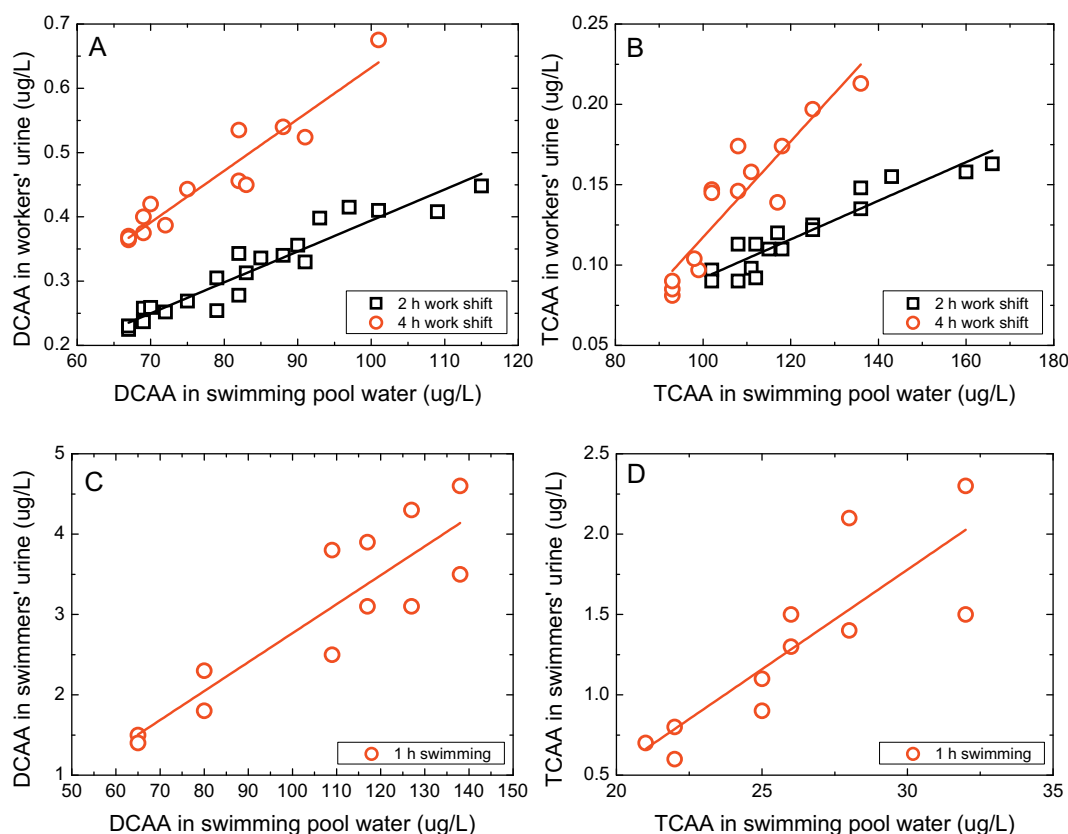


Fig. 6. The relationship between HAA concentrations in SPWs and human urine. Data are from (Cardador and Gallego, 2011; Cardador and Gallego, 2010).

#### 4.1.3. Other DBPs

Apart from these commonly mentioned regulated DBPs (i.e., THMs and HAAs), other DBPs in SPWs may also have the potential to be absorbed via human skin during swimming. For example, Xiao et al. (2012) newly identified some halo(nitro)phenols in SPWs, among which 2,4-dibromophenol, 2,4-dichlorophenol, and 2-bromophenol have the skin permeability of 0.031, 0.021, and 0.023 cm/h, respectively. Haloketones have a skin permeation range of 0.024–0.043 cm/h which is more than one order of magnitude higher than HAAs (0.001–0.003 cm/h) (Xu et al., 2002). The permeability of haloketones triples with the temperature increased from 20 to 40 °C. These permeation studies may further promote researchers' interests of quantifying these unregulated DBPs in human matrix for exposure estimation. A comprehensive identification and characterization of DBP mixture in SPWs is essential for human exposure assessment.

#### 4.2. The relevance between pool activities and health risks

Health risks of pool activities are commonly assessed by the association with THMs due to their sufficient data availability. The prevalence of health symptoms including red eyes, itchy eyes, dyspnea/asthma, and blocked nose was positively linked to THM concentration in alveolar air ( $> 21 \mu\text{g}/\text{m}^3$ ) based on a survey in twenty indoor pools (Fantuzzi et al., 2010). Kogevinas et al. (2010) mentioned that urine mutagenicity correlated proportionally with exhaled  $\text{CHBr}_3$  ( $p = 0.004$ ) and the frequency change of micronucleated lymphocytes correlated with Br-THMs ( $p \leq 0.05$ ). Rahman et al. (2010) found that the increase of THM concentration and exposure duration enhanced the risk of colorectal cancer. Panyakapo et al. (2008) assessed the cancer risk of swimmers exposed to THM-contaminated SPWs as  $7.99 \times 10^{-4}$  in average which exceeds the acceptable level based on U.S. EPA standard, while only  $2.19 \times 10^{-5}$  for non-swimmers. Lee et al. (2009) assessed

the lifetime cancer risk via THM inhalation during swimming in a range of  $7.77 \times 10^{-4}$  to  $1.36 \times 10^{-3}$  based on a study of 183 indoor swimming pools in Korea. The cancer risk via THM exposure was attributed mainly by swimming activities (~94.2%), compared to a relatively low percentage of 4.1% for tap water intake (Panyakapo et al., 2008). Similarly, Chowdhury (2015) found that the cancer risk of THM exposure in SPWs was more than four times higher than that in DWs. Villanueva et al. (2007b) reported 23% of the total THM uptake from swimming and only 1% from DWs for pregnant women.

Pool attendants are eventually exposed to a mixture of varieties of DBPs in aqueous and gaseous phases during pool activities. Many researchers directly assessed the relevance of health symptoms with pool activities. Suffering of dermatitis by swimmers in brominated swimming pools has been reported (Pardo et al., 2007). Fantuzzi et al. (2010) conducted a survey to record the declared health symptoms (e.g., ocular, cutaneous, asthma-related and other respiratory symptoms) among pool workers. It showed that workers in swimming pools suffered frequently from cold (65.4%), sneezing (52.6%), red eyes (48.9%) and itchy eyes (44.4%). Workers with the frequent touch of SPWs, e.g., lifeguards and trainers, were much easier to catch symptoms like red eyes, runny nose, voice loss and cold, than other pool employees (e.g., office and cafe). Villanueva and Font Ribera (2012) pointed out that pool participants had higher risks of suffering bladder cancer and asthma. Villanueva et al. (2007a) found that the risk of suffering bladder cancer increased with swimming activities and the duration of exposure to THM-contaminated water. Bernard et al. (2008) similarly found that the increase of exposure time in pools increased the prevalence of asthma, respiratory allergies or airways inflammation for the adolescents. However, Font-Ribera et al. (2009) pointed out that swimming pool attendance in childhood was associated with slightly lower prevalence of current asthma. The controversial association between swimming activities and health risks needs further investigation.



A comprehensive consideration of all existed DBPs in SPWs and their associated health effects will be of great importance for the overall risk assessment.

## 5. DBP treatment

The high frequency of occurrence and high concentration of DBPs in SPWs demonstrate that the conventional pool water treatment system (flocculation-sand filtration-chlorination) cannot effectively remove DBPs or DBP precursors to achieve good water quality. Some novel DBP control processes, such as membrane filtration, AOPs, and biodegradation, are beneficial to improve the chemical safety of pool participates. In this section, we review several advanced DBP treatment approaches reported in the past two decades.

### 5.1. Membrane filtration

Membrane has been widely used in the water and wastewater treatment and seawater desalination with its maturely developed technology and operation. The enhanced safety awareness towards DBPs in recent years promotes membrane filtration as a potential technology for DBP treatment. Laboratory experiments reveal that DBP treatment by forward osmosis (FO), nanofiltration (NF), and reverse osmosis (RO) has achieved good results. Kong et al. (2014) for the first time used FO to treat 9 HAAs and found that the rejection of each HAA reached > 94.6% for the orientation of active layer facing the feed water using 1 mol/L NaCl as the draw solution. The rejection of five regulated HAAs reached 90–100% by a dense negatively charged NF membrane (Chalatip et al., 2009). Kimura et al. (2003) found 91–96% of DCAA and TCAA were removed by NF/RO membranes. Yang et al. (2017a) also showed that the rejection of 9 HAAs reached equal or higher than 90% by commercial NF/RO membranes (XLE, NF90 and SB50). At usual solution pHs of SPWs (7.2–7.8), RO/NF membranes, typically of polyamide or cellulose acetate chemistry, are generally negatively charged. HAAs with pKa values between 0.05 and 2.73 are present mainly in the form of HAA anions. The charge repulsion between membranes and HAAs, in addition to size exclusion, contributes significantly to the consistently high HAA rejection in the above studies. Uyak et al. (2008) found that the rejection of total THMs reached as high as 95% by NF membranes. The rejection of individual THM followed the order of  $\text{CHClBr}_2 > \text{CHCl}_2\text{Br} > \text{CHCl}_3$ , attributed to the role of the molecular size. Xu et al. (2005) found that high initial rejections of  $\text{CHCl}_3$  (> 80%) and  $\text{CHBr}_3$  (> 90%) by 3 NF/RO membranes was attributed to the effect of adsorption (hydrophobic-hydrophobic solute-membrane interactions) in addition to size exclusion. The rejections were reduced to 20–35% and 35–45%, respectively, at steady state conditions. Doederer et al. (2014) reported a wide range of rejections (i.e., 5–100%) for 29 DBPs (e.g., THMs, I-THMs, HANs, HNMs, chloral hydrate, halo ketones, and haloacetamides) by NF/RO membranes. These rejection data correlated well with the intrinsic DBP molecular properties (e.g., polar surface area, molecular volume, molecular weight, dipole moment, etc.) and operational parameters (e.g., temperature and flux) by a multiple linear regression method. Molecular properties were found to have greater impacts on DBP rejection than operational parameters (polar surface area > molecular volume > dipole moment > temperature > flux).

In addition to bench-scale experiments, Klüpfel et al. (2011) applied NF with the membrane installed at the outlet of a traditional sand filter in a by-pass to investigate its effect on a large pool. The rejections of DBPs and DBP precursors reached as high as 80% and 70%, respectively. High rejections (86–94%) for charged HAAs and low rejections (as low as 55%) for neutral and low-molecular-weight DBPs (e.g.,  $\text{CHCl}_3$  and  $\text{CHBrClCN}$ ) were shown in a pilot-scale RO plant in California (Agus and Sedlak, 2010). Fujioka et al. (2012) reviewed NDMA removal based on the findings in some laboratory-, pilot- and full-scale RO plants and found significantly different rejections (from negligible up to

86%) caused by the varied operating parameters, e.g., feed solution temperature and pH, ionic strength, and membrane permeate flux.

Removal of DBP precursors by membrane filtration could be an effective method to minimize DBP formation at source. Sentana et al. (2010) found that NF membranes reduced the formation potential of HAAs and THMs (deemed as HAA-FP and THM-FP) by > 82%. The rejection of THM and HAA precursors reached 77–96% and 75–92%, respectively, by NF membranes under optimized conditions (Chellam, 2000). However, the high TOC rejection (71–94%) coupled with the extremely low bromide rejection (< 10%) shifted Cl-DBPs to Br-DBPs upon chlorination to permeate water (Chellam, 2000).

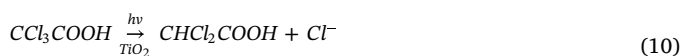
Existing studies demonstrate the potential of using membrane filtration for DBP treatment in SPWs. However, there are still several critical aspects to be further addressed: 1) the commonly used polyamide-based membranes show high DBP rejections but are sensitive to chlorine which is ubiquitously present in SPWs (Do et al., 2012a; Do et al., 2012b, c; Klüpfel et al., 2011). 2) The DBP concentrations used in laboratory experiments varied significantly which may produce completely different rejections. 3) The SPW matrix with the co-presence of dissolved organic matter and divalent cations (e.g., calcium) may lead to severe organic fouling and finally affect DBP rejection. 4) Special attention should be paid to the further treatment of DBP-accumulated retentate generated from the filtration process. Addressing these concerns will assist the full application of membrane technology for DBP treatment in SPWs.

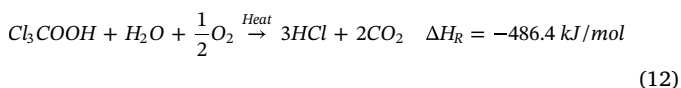
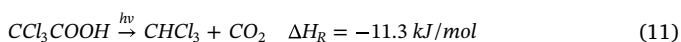
### 5.2. Advanced oxidation processes

The application of AOPs in the SPW treatment, often involving the use of UV,  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  to generate hydroxyl radicals ( $\cdot\text{OH}$ ) for the degradation of organic matter, is promising to eliminate DBPs and DBP precursors.

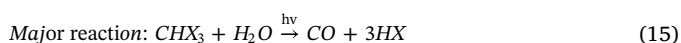
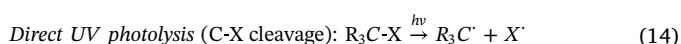
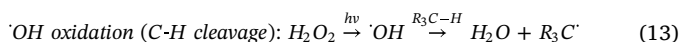
Direct sunlight is an economic natural source for DBP degradation in outdoor pools. Chen et al. (2010) investigated the photolysis of a variety of DBPs under natural solar irradiation and found that the stability of DBPs generally followed the order of N-DBPs < C-DBPs, Br-, I-DBPs < Cl-DBPs, T-DBPs < D-DBPs < M-DBPs (T-, D-, M-DBPs refer to tri-halogenated, di-halogenated, and mono-halogenated DBPs respectively). Some THMs and HAAs showed high persistence to solar irradiation. For example, 5–10% of THMs was removed after 6 h solar exposure (1150–1300  $\text{W/m}^2$  irradiation intensities), revealing that solar photolysis is insufficient for the degradation of these DBPs. It partly explains the high concentrations of DBPs especially non-volatile HAAs detected in outdoor pools (see Tables 5 and 6). The fate of  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{ICl}$ , and  $\text{CH}_2\text{IBr}$  under natural solar photolysis demonstrated that one iodide was substituted by one chlorine (Jones and Carpenter, 2005).

DBPs exposed under UV or visible light in the presence of catalyst undergo good photocatalysis degradation. Lifongo et al. (2004) found that HAAs had better photocatalysis degradation under visible light ( $\lambda > 400$ ) in the presence of  $\text{TiO}_2$ , compared to photolysis only (without  $\text{TiO}_2$ ). HAAs with a higher number of halogens had higher degradation rate constants and no obvious photolysis was observed for mono-halogen HAAs. Dehalogenation of HAAs was the main mechanism since the halide ions were produced during the reactions (for example, TCAA may be degraded to form DCAA and chloride ions (Eq. (10))). HAAs under high temperatures underwent thermal degradation as well (Lifongo et al., 2004). Spangenberg et al. (1996) have proposed two possible degradation mechanisms for TCAA: 1) photolysis by radical decarboxylation to form  $\text{CHCl}_3$  and  $\text{CO}_2$  (Eq. (11)); 2) pyrolysis by dehalogenation to form  $\text{HCl}$  and  $\text{CO}_2$  (Eq. (12)). The commonly used metal catalysts (e.g. Cu, Fe, Mn, Ti, V, Mo and Zn) showed no direct effect for HAA degradation (Lifongo et al., 2010).





UV/H<sub>2</sub>O<sub>2</sub> based AOPs are widely used in the treatment of DBPs. Rudra et al. (2005) found that 70 min UV irradiation completely degraded THMs except for CHCl<sub>3</sub> (46% removal) using an initial concentration of 50 µg/L for each THM. The addition of 0.1% H<sub>2</sub>O<sub>2</sub> significantly enhanced CHCl<sub>3</sub> degradation to 92%. However, only 10–12% THMs were removed by 0.1% H<sub>2</sub>O<sub>2</sub> solution without UV exposure, indicating sole H<sub>2</sub>O<sub>2</sub> to be a mild oxidizer. The UV/H<sub>2</sub>O<sub>2</sub> provides oxidation via ·OH generation by H<sub>2</sub>O<sub>2</sub> photolysis, which is consistent with ·OH dependent degradation of Cl-DBPs (Eq. (13)) (Jo et al., 2011; Rudra et al., 2005). Jo et al. (2011) found that the removal of Br-THMs and Br-HAAs reached > 80% at a UV dose of 1200 mJ/cm<sup>2</sup> in the presence of 6 mg/L H<sub>2</sub>O<sub>2</sub> and the removal efficiency increased with the increased bromine number in the molecules, e.g., CHBr<sub>3</sub> > CHBr<sub>2</sub>Cl and TBAA > DBAA. The degradation of Br-DBPs mainly rely on UV hydrolysis (see Eq. (14), where X refers to a halogen atom) in the UV/H<sub>2</sub>O<sub>2</sub> process. This UV hydrolysis mechanism is attributed to high UV absorption by Br-DBPs and enough energy from UV photon (113 kcal/mol at 253.7 nm) for the cleavage of C–Br bond (70.4 kcal/mol for CHBr<sub>3</sub>) (Jo et al., 2011). Xiao et al. (2014) performed degradation experiments of I-THMs by UV 254 irradiation. The I-THMs underwent a rapid first-order photodegradation process via the cleavage of carbon-halogen bond, with reaction rate constants (in the range of 0.1–0.6 min<sup>−1</sup>) proportional to their corresponding molar extinction coefficients (an indicator of UV absorption). End-product identification revealed that THMs were mainly converted to hydrogen halide (92–109% recovery) and also produced minor HCOOH (5% carbon conversion) as shown in Eqs. (15) and (16). Similar observation was reported by Kwok et al. (2004). The degradation rate constants of I-THMs in UV/H<sub>2</sub>O<sub>2</sub> system increased to > 2 min<sup>−1</sup>, indicating the ·OH promoted photolysis in addition to direct UV photolysis (Xiao et al., 2014). The combined UV radiation and ultrasound sonolysis (UV-US) showed a greater degradation rate for TCAA than UV or US alone, attributed to dual effects of free radical excitation by UV and thermal degradation by US (Wu et al., 2001). NDMA was degradable under UV with a reaction rate constant up to 0.36 min<sup>−1</sup> (Sharpless and Linden, 2003). While in the presence of chlorinated dimethylamine and monochloramine, UV irradiation contributes to simultaneous NDMA photolysis and formation (Soltermann et al., 2013). Although the addition of H<sub>2</sub>O<sub>2</sub> to UV treatment has usually been applied to improve NDMA removal, Sharpless and Linden (2003) reported that the addition of H<sub>2</sub>O<sub>2</sub> slightly assisted or seriously hindered NDMA degradation due to the competing effects of light screening by H<sub>2</sub>O<sub>2</sub> and ·OH promoted NDMA degradation.



Some unregulated but potentially more toxic nitrogenous DBPs are degradable by AOPs as well. HNMs underwent homolysis or heterolysis to produce halides, nitrite, nitrate, and/or carbon dioxide under UV254 radiation (Fang et al., 2013). Neutral to alkaline pHs which are typical for SPWs, contribute to HNM degradation due to their high UV molar absorptivity at these pHs. Two nitrogenous DBPs, *N*-nitrosopyrrolidine and *N*-nitrosopiperidine, were almost completely photodegraded (> 99%) after only 5 min UV 254 exposure (Xu et al., 2009). The N–N bond fission of these two compounds was proposed as the first

photodegradation step followed by the further degradation to form aliphatic amines.

AOPs are also used to reduce the amount of DBP precursors and thus control the DBPs in the treated water. Combined AOPs, i.e., O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, showed better elimination of DBP precursors (using TOC, AOX-FP, THM-FP, and/or HAA-FP as indicators) than O<sub>3</sub> and UV alone for both SPW and surface water treatment (Chin and Bérubé, 2005; Glauner et al., 2005a). The removal efficiency of TOC, THM-FP and HAA-FP after 1 h O<sub>3</sub>/UV treatment reached 50%, 80% and 70%, respectively, and reaction rate constants were 0.04, 0.12 and 0.15 min<sup>−1</sup>, respectively (Chin and Bérubé, 2005). Wang et al. (2000) found UV/H<sub>2</sub>O<sub>2</sub> as an effective method for the remediation of a group of important DBP precursors, i.e., humic acids (~90% removal within 1 h with a reaction rate constant of 0.037 min<sup>−1</sup>).

In conclusion, considerable laboratory studies reviewed above have demonstrated the effectiveness of AOPs used for DBP degradation via means of dehalogenation, decarboxylation, and others, depending on the specific AOPs and DBP species. Nevertheless, there are still some important concerns or limitations we need to pay attention to. It is essential to optimize H<sub>2</sub>O<sub>2</sub> dosage to the UV/H<sub>2</sub>O<sub>2</sub> system as an excess addition may result in a scavenging effect to the hydroxyl radical or light screening, eventually decreases the removal efficiency of DBPs or DBP precursors (Jo et al., 2011; Rudra et al., 2005; Sharpless and Linden, 2003; Wang et al., 2000). Humic acids, nitrate, chloride, and sulphate commonly detected in SPWs may affect the DBP photodegradation efficiency via shielding or activating ·OH (Chen et al., 2010; Xiao et al., 2014). In addition, the application of medium-pressure UV lamps in an indoor chlorinated public swimming pool could even result in a significant increase of THMs, particularly CHCl<sub>3</sub> and CHBrCl<sub>2</sub>, due to the increase in active chlorine and radical initiation by UV radiation (Cassan et al., 2006). Therefore, the systematic understanding of real SPW characteristics and the fundamental reaction mechanisms are critical to ensure the effective AOP applications in real SPWs. Furthermore, the comprehensive identification of end-products after AOPs is essential as DBPs are commonly degraded to a variety of small weight compounds with unknown or even higher toxicity (Glauner et al., 2005b; Xu et al., 2009). Hence, it is far from enough to obtain a high degradation rate. An overall risk assessment for the degradation process is essential.

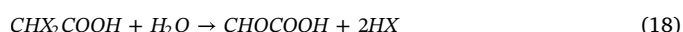
### 5.3. Biodegradation

Biodegradation is another potential technique for the removal of DBPs in water systems. HAAs are shown to be biodegradable under conditions of interest (Chuang et al., 2011; Pluchon et al., 2013; Tung and Xie, 2009). Chlorine < 0.3 mg/L and heterotrophic bacteria > 10,000 HPC/mL were necessary conditions for effective HAA removal (Chuang et al., 2011; Tung and Xie, 2009). Chuang et al. (2011) observed the removal of MCAA and DCAA reached up to 80% by sand filtration. The bioactivity on the sand surface made a significant contribution to the HAA removal due to the biofilm development under perennial high temperature. Nevertheless, Yang et al. (2016) still observed an average HAA concentration of ~1000 µg/L in a public campus pool treated with sand filtration. These contradictory findings might be explained by the difference of chlorine residuals in these two systems. The average chlorine concentration of 0.57 mg/L in the campus pool in Yang's study (higher than the threshold 0.5 mg/L) may deactivate the corresponding bio-degraders and thus prevent effective HAA biodegradation (Chuang et al., 2011). The inverse relationship between heterotrophic bacteria and HAA concentrations under low chlorine concentration further emphasized the important role of bacteria for HAA degradation (Tung and Xie, 2009). Bacteria, e.g., *S. natatoria* and *P. donghaensis*, have been isolated and proven to be responsible for HAA degradation (Chuang et al., 2011). Other parameters including water temperature, retention time, the composition of organic matter, etc., also affect HAA degradation (Pluchon et al., 2013).

On the contrary, biodegradation may be far less effective for THMs. A recent study by [Tung and Xie \(2009\)](#) even reported a proportional relationship between bacteria and THM concentration in some water distribution systems. The application of DBP biodegradation in SPWs still has a long way to go. The specific SPW matrix in particular constant high chlorine (e.g., 1–3 mg/L) may inhibit the growth of some contributing bacteria. It is worthwhile to find robust bacteria which are DBP biodegradable and stable under high chlorine conditions.

#### 5.4. Thermal degradation and chemical reduction

[Lifongo et al. \(2010\)](#) explored the thermal degradation of HAAs and found trihalogenated haloacetic acids (T-HAAs) were degraded by decarboxylation (as shown in Eq. (11) for TCAA), via C–C bond crack. The higher activation energy of decarboxylation reaction (C–C break) for TCAA compared to TBAA (151 vs. 139 kJ/mol/k) was consistent to its lower reaction rate constant ( $4.80 \times 10^{-10}$  vs.  $7.77 \times 10^{-8} \text{ s}^{-1}$ , at 15 °C). Monohalogenated and dihalogenated haloacetic acids (M-HAAs, D-HAAs) were hydrolysed via oxygen attack to the  $\alpha$ -carbon of the molecules, producing glycolic and glyoxalic acids, and its corresponding hydrogen halide (as shown in Eqs. (17) and (18), X represents halogens). The reaction rate for decarboxylation followed an order of T-HAAs > D-HAAs > M-HAAs, as halogen attachment to the  $\alpha$ -carbon weakens the C–C bond. [Zhang and Minear \(2002\)](#) found the temperature-dependent decomposition of T-HAAs produce the corresponding THMs via decarboxylation.



Zero-valent iron ( $\text{Fe}^0$ ) in the iron pipe system is an effective substance to degrade HAAs by dehalogenation ([Hozalski et al., 2001](#); [Tang et al., 2013](#)). Debromination happened prior to dechlorination for the mixed chloro-bromo species, e.g., BDCAA, and therefore Br-HAAs were much easier to be removed than chlorinated ones (reaction rate constants followed  $\text{BDCAA} > \text{CDBAA} \approx \text{TBAA} \gg \text{TCAA}$  as shown in Table 7) ([Hozalski et al., 2001](#)). [Tang et al. \(2013\)](#) found that DCAA and MCAA as the subsequent dehalogenation products of TCAA by  $\text{Fe}^0$  were completely biodegraded via a subsequent active carbon treatment process with a retention time of 10 min. [Korshin and Jensen \(2001\)](#) observed complete dehalogenation of Br-HAAs and partial dehalogenation of Cl-HAAs (produced notable MCAA whose direct reduction was difficult) by an electrochemical reduction method using copper or gold as the electrode. Other DBPs, e.g., chloropicrin, trichloroacetonitrile, and dibromoacetonitrile, also underwent dehalogenation in the presence of sulphite as a reductant ([Croue and Reckhow, 1989](#)).

**Table 7**  
HAA degradation rate constant.

	HAA degradation rate constant ( $\text{min}^{-1}$ )									References
	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA	
Solar photolysis	3.48E–05	1.87E–04	1.18E–05	4.00E–06	6.34E–05	3.48E–04	2.20E–05	1.18E–04	6.34E–04	(Chen et al., 2010)
Photocatalysis by solar light + $\text{TiO}_2$	1.15E–05	7.68E–06	4.61E–05	7.68E–05	2.69E–05	3.46E–05			5.76E–05	
AOP by $\text{H}_2\text{O}_2$ + UV	3.48E–02	6.60E–02	3.00E–02	1.74E–02		7.80E–01			3.84E+00	(Jo et al., 2011)
AOP by UV		1.26E–01				9.00E–01			4.44E+00	(Jo et al., 2011)
Biodegradation by rapid sand filtration	1.70E–01		1.50E–01							(Chuang et al., 2011)
Reduction and biodegradation by $\text{Fe}^0$ + BAC	4.00E–01		4.00E–01	5.00E–01						(Tang et al., 2013)
Reduction by $\text{Fe}^0$				1.33E–03			1.77E–01	2.38E–02	2.35E–02	
Thermal degradation at 82–83 °C	8.94E–05	1.39E–03	2.69E–05		2.36E–04	1.78E–04				(Lifongo et al., 2010)

#### 5.5. Hybrid process

The investigation of multi-stage DBP purification in SPWs is of great interests. For a municipal swimming pool in France, a hybrid process (hollow fibre ultrafiltration (UF) + granular activated carbon adsorption) was included after a conventional SPW treatment system (coagulation-sand filtration-disinfection) ([Barbot and Moulin, 2008](#)). This 18-month study illustrated that the hybrid process limited the combined chlorine (as an indicator of DBPs) to be lower than 0.35 mg/L. [Glauner et al. \(2005b\)](#) used a two-step membrane filtration (UF followed by NF) to separate the compounds into three categories, i.e., < 200, 200–1000, > 1000 g/mol. DBPs with molecular weight < 1000 g/mol accounted for > 80% in both indoor and outdoor SPWs. The extract with lower molecular weight had higher genotoxicity. It is essential to use membranes with molecular weight cut-offs (MWCOs) < 200 g/mol to minimize its potential toxicity. Meanwhile, [Glauner et al. \(2005a\)](#) also attempted to apply UF or NF prior to AOPs for the treatment of SPWs and found that the overall eliminations of DBPs and DBP precursors reached up to 80%. The  $\text{Fe}^0$ -active carbon treatment process contributed to TCAA dehalogenation by  $\text{Fe}^0$  and the subsequent complete biodegradation of DCAA and MCAA (as the dehalogenated products of TCAA) by active carbon within 10 min ([Tang et al., 2013](#)). The hybrid processes can potentially substitute or supplement the conventional SPW treatment process to achieve better water quality. However, a full-scale application needs further validation, e.g., the stability of long-term operation, membrane fouling-induced side-effects.

## 6. Conclusions

Previous research has mainly focused on the DBPs in the context of DWs subject to regulations by some global organizations or local government (e.g., EPA, WHO). Unlike DWs, SPWs are more complicated and may present higher DBP-related health risks due to the multi-various organic inputs from the bathers (body fluids and PCPs) in addition to NOM from source water. This paper critically reviewed the latest research progress on the regulation, formation, exposure, and treatment of DBPs in the context of SPWs, with a total of ~200 references. DBPs in SPWs, with the main focus on HAAs and THMs, are often much or several orders of magnitude higher than the MCLs in DWs or SPWs. A more comprehensive DBP identification targeting at SPW context is necessary. Swimmers and workers are exposed to THMs mainly via dermal absorption and inhalation and HAAs via ingestion, reflecting by DBPs detected in human matrix including exhaled air, urine, blood, and plasma. Membrane filtration, AOPs, biodegradation, thermal degradation, chemical reduction, and some hybrid processes are the latest approaches for the control and treatment of DBPs. The



removal efficiency, possible mechanisms and future challenges of these DBP treatment methods have been discussed to facilitate their full-scale applications and to provide potential directions for further research roadmap.

## Acknowledgements

L. Yang receives her scholarship from Interdisciplinary Graduate School (IGS) at Nanyang Technological University (NTU), Singapore. The authors also acknowledge Residues and Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute (NEWRI) in NTU for the financial support.

## References

- Affifi, M.Z., Blatchley III, E.R., 2015. Seasonal dynamics of water and air chemistry in an indoor chlorinated swimming pool. *Water Res.* 68, 771–783.
- Aggazzotti, G., Righi, E., Fantuzzi, G., Biasotti, B., Ravera, G., Kanitz, S., Barbone, F., Sansebastiano, G., Battaglia, M.A., Leoni, V., Fabiani, L., Triassi, M., Sciacca, S., 2004. Chlorination by-products (CBPs) in drinking water and adverse pregnancy outcomes in Italy. *J. Water Health* 2 (4), 233–247.
- Agus, E., Sedlak, D.L., 2010. Formation and fate of chlorination by-products in reverse osmosis desalination systems. *Water Res.* 44 (5), 1616–1626.
- Alcudia-León, M.C., Lucena, R., Cárdenas, S., Valcárcel, M., 2013. Determination of parabens in waters by magnetically confined hydrophobic nanoparticle micro-extraction coupled to gas chromatography/mass spectrometry. *Microchem. J.* 110, 643–648.
- ANSES, 2012. Health Risk Assessment in Swimming Pools. Part 1: Regulated Pools.
- ANSES, 2014. Health Risk Assessment in Swimming Pools. Part 2: Whirlpool.
- Apra, M.-C., Banchi, B., Lunghini, L., Pagliantini, M., Peruzzi, A., Sciarra, G., 2010. Disinfection of swimming pools with chlorine and derivatives: formation of organo-chlorinated and organobrominated compounds and exposure of pool personnel and swimmers. *Nat. Sci.* 2 (02), 68.
- Arnaud, C.H., 2016. The chemical reactions taking place in your swimming pool. *Chem. Eng. News* 94 (31), 28–32.
- Askins, A., 2013. Cyanuric Acid in Commercial Swimming Pools and its Effects on Chlorine's "Staying Power" and Oxidation Reduction Potentials. (Master thesis).
- Bader, E.L., Hrudey, S.E., Froese, K.L., 2004. Urinary excretion half life of trichloroacetic acid as a biomarker of exposure to chlorinated drinking water disinfection by-products. *Occup. Environ. Med.* 61 (8), 715–716.
- Balmer, M.E., Buser, H.-R., Müller, M.D., Poiger, T., 2005. Occurrence of some organic UV filters in wastewater, in surface waters, and in fish from Swiss lakes. *Environ. Sci. Technol.* 39 (4), 953–962.
- Barbot, E., Moulin, P., 2008. Swimming pool water treatment by ultrafiltration–adsorption process. *J. Membr. Sci.* 314 (1–2), 50–57.
- Beach, H., 1971. Composition and Concentrative Properties of Human Urine.
- Bernard, A., Carboneille, S., de Burbure, C., Michel, O., Nickmilder, M., 2006. Chlorinated pool attendance, atopy, and the risk of asthma during childhood. *Environ. Health Perspect.* 114 (10), 1567–1573.
- Bernard, A., Nickmilder, M., Voisin, C., 2008. Outdoor swimming pools and the risks of asthma and allergies during adolescence. *Eur. Respir. J.* 32 (4), 979–988.
- Blatchley III, E.R., Cheng, M., 2010. Reaction mechanism for chlorination of urea. *Environ. Sci. Technol.* 44 (22), 8529–8534.
- Borges, E.P., Lavorante, A.F., Reis, B.F.d., 2005. Determination of bromide ions in seawater using flow system with chemiluminescence detection. *Anal. Chim. Acta* 528 (1), 115–119.
- Bottoni, P., Bonadonna, L., Chirico, M., Caroli, S., Záray, G., 2014. Emerging issues on degradation by-products deriving from personal care products and pharmaceuticals during disinfection processes of water used in swimming pools. *Microchem. J.* 112, 13–16.
- Boudenne, J.L., Parinet, J., Demelas, C., Manasfi, T., Coulomb, B., 2017. Monitoring and factors affecting levels of airborne and water bromoform in chlorinated seawater swimming pools. *J. Environ. Sci.* 58, 262–270.
- Bougeard, C.M.M., Janmohamed, I.H.S., Goslan, E.H., Jefferson, B., Watson, J.S., Morgan, G.H., Parsons, S.A., 2008. Disinfection By-products in Drinking Water. American Chemical Society, pp. 95–108.
- Cammann, K., Hübner, K., 1993. False results in headspace—gas chromatographic analysis of trihalomethanes in swimming pool water due to elevated headspace temperatures. *J. Chromatogr. A* 648 (1), 294–298.
- Cammann, K., Hübner, K., 1995. Trihalomethane concentrations in swimmers' and bath attendants' blood and urine after swimming or working in indoor swimming pools. *Arch. Environ. Health Int. J.* 50 (1), 61–65.
- Cardador, M.J., Gallego, M., 2010. Determination of haloacetic acids in human urine by headspace gas chromatography-mass spectrometry. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 878 (21), 1824–1830.
- Cardador, M., Gallego, M., 2011. Haloacetic acids in swimming pools: swimmer and worker exposure. *Environ. Sci. Technol.* 45 (13), 5783–5790.
- Caro, J., Gallego, M., 2007. Assessment of exposure of workers and swimmers to trihalomethanes in an indoor swimming pool. *Environ. Sci. Technol.* 41 (13), 4793–4798.
- Caro, J., Gallego, M., 2008. Alveolar air and urine analyses as biomarkers of exposure to trihalomethanes in an indoor swimming pool. *Environ. Sci. Technol.* 42 (13), 5002–5007.
- Caro, J., Serrano, A., Gallego, M., 2007. Sensitive headspace gas chromatography–mass spectrometry determination of trihalomethanes in urine. *J. Chromatogr. B* 848 (2), 277–282.
- Cassan, D., Mercier, B., Castex, F., Rambaud, A., 2006. Effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool. *Chemosphere* 62 (9), 1507–1513.
- Catto, C., Sabrina, S., Gnette, C.-T., Manuel, R., Robert, T., 2012. Occurrence and spatial and temporal variations of disinfection by-products in the water and air of two indoor swimming pools. *Int. J. Environ. Res. Public Health* 9 (8), 2562–2586.
- CDPHE, 1998. State Board of Health Regulations Pertaining to Swimming Pools and Mineral Baths. Colorado Department of Public Health and Environment. Water Quality Control Division.
- CDW, 2014. Guidelines for Canadian Drinking Water Quality. Federal-Provincial-Territorial Committee on Drinking Water of the Federal-Provincial-Territorial Committee on Health and the Environment.
- Chalatip, R., Chawalit, R., Nopawan, R., 2009. Removal of haloacetic acids by nanofiltration. *J. Environ. Sci.* 21 (1), 96–100.
- Cheema, W.A., Manasfi, T., Kaarsholm, K.M.S., Andersen, H.R., Boudenne, J.L., 2017. Effect of medium-pressure UV-lamp treatment on disinfection by-products in chlorinated seawater swimming pool waters. *Sci. Total Environ.* 599, 910–917.
- Chellam, S., 2000. Effects of nanofiltration on trihalomethane and haloacetic acid precursor removal and speciation in waters containing low concentrations of bromide ion. *Environ. Sci. Technol.* 34 (9), 1813–1820.
- Chen, B., Lee, W., Westerhoff, P.K., Krasner, S.W., Herckes, P., 2010. Solar photolysis kinetics of disinfection byproducts. *Water Res.* 44 (11), 3401–3409.
- Chen, M.J., Lin, C.H., Duh, J.M., Chou, W.S., Hsu, H.T., 2011. Development of a multi-pathway probabilistic health risk assessment model for swimmers exposed to chloroform in indoor swimming pools. *J. Hazard. Mater.* 185 (2–3), 1037–1044.
- Chin, A., Bérubé, P.R., 2005. Removal of disinfection by-product precursors with ozone-UV advanced oxidation process. *Water Res.* 39 (10), 2136–2144.
- Chowdhury, S., 2015. Predicting human exposure and risk from chlorinated indoor swimming pool: a case study. *Environ. Monit. Assess.* 187 (8), 502.
- Chowdhury, S., Alhooshani, K., Karanfil, T., 2014. Disinfection byproducts in swimming pool: occurrences, implications and future needs. *Water Res.* 53, 68–109.
- Chu, H., Nieuwenhuijsen, M., 2002. Distribution and determinants of trihalomethane concentrations in indoor swimming pools. *Occup. Environ. Med.* 59 (4), 243–247.
- Chuang, Y.H., Wang, G.S., Tung, H.H., 2011. Chlorine residuals and haloacetic acid reduction in rapid sand filtration. *Chemosphere* 85 (7), 1146–1153.
- Cimetiere, N., De Laat, J., 2014. Effects of UV-dechloramination of swimming pool water on the formation of disinfection by-products: a lab-scale study. *Microchem. J.* 112, 34–41.
- Craun, G., Calderon, R., Craun, M., 2005. Outbreaks associated with recreational water in the United States. *Int. J. Environ. Health Res.* 15 (4), 243–262.
- Croue, J.P., Reckhow, D.A., 1989. Destruction of chlorination byproducts with sulfite. *Environ. Sci. Technol.* 23 (11), 1412–1419.
- De Laat, J., Feng, W., Frey, D.A., Dossier-Berne, F., 2011. Concentration levels of urea in swimming pool water and reactivity of chlorine with urea. *Water Res.* 45 (3), 1139–1146.
- DIN, 2012. Treatment of the Water of Swimming Pools and Baths - Part 1: General Requirements. Germany Standard DIN 19643-1: 2012-11.
- Directive, E., 1998. EU Directive 98/83/EC of 3 November.
- Do, V.T., Reinhard, M., Tang, C.Y., Leckie, J.O., 2012a. Effects of hypochlorous acid exposure on the rejection of salt, polyethylene glycols, boron and arsenic(V) by nanofiltration and reverse osmosis membranes. *Water Res.* 46 (16), 5217–5223.
- Do, V.T., Tang, C.Y., Reinhard, M., Leckie, J.O., 2012b. Degradation of polyamide nanofiltration and reverse osmosis membranes by hypochlorite. *Environ. Sci. Technol.* 46 (2), 852–859.
- Do, V.T., Tang, C.Y., Reinhard, M., Leckie, J.O., 2012c. Effects of chlorine exposure conditions on physicochemical properties and performance of a polyamide membrane-mechanisms and implications. *Environ. Sci. Technol.* 46 (24), 13184–13192.
- Doederer, K., Farré, M.J., Pidou, M., Weinberg, H.S., Gernjak, W., 2014. Rejection of disinfection by-products by RO and NF membranes: influence of solute properties and operational parameters. *J. Membr. Sci.* 467, 195–205.
- DPH, 2013. Rules and Regulations. Swimming Pools, Spa and Recreational Water Parks, Chapter 511-3-5. Georgia Department of Public Health. <http://pooloperationmanagement.com/about/locations/georgia/>.
- Dyck, R., Sadiq, R., Rodriguez, M.J., Simard, S., Tardif, R., 2011. Trihalomethane exposures in indoor swimming pools: a level III fugacity model. *Water Res.* 45 (16), 5084–5098.
- Ekowati, Y., Buttiglieri, G., Ferrero, G., Valle-Sistac, J., Diaz-Cruz, M.S., Barcelo, D., Petrovic, M., Villagrasa, M., Kennedy, M.D., Rodriguez-Roda, I., 2016. Occurrence of pharmaceuticals and UV filters in swimming pools and spas. *Environ. Sci. Pollut. Res.* 23 (14), 14431–14441.
- EPA, U., 1979. National Interim Primary Drinking Water Regulations: Control of Trihalomethanes in Drinking Water: Final Rules. 44. pp. 68624–68705.
- EPA, U., 1998. National Primary Drinking Water Regulations: Disinfectants and Disinfection byproducts; Final Rule. 63. pp. 69390–69476.
- EQA, 2016. Regulation Respecting Water Quality in Swimming Pools and Other Artificial Pools. Environment Quality Act. <http://legisquebec.gouv.qc.ca/en/ShowDoc/cr/Q-2,%20r.%2039>.
- Erdinger, L., Kirsch, F., Sonntag, H.G., 1998. Irritating effects of disinfection by-products in swimming pools. *Zentralbl. Hyg. Umweltmed.* 200 (5–6), 491–503.
- Erdinger, L., Kühn, K.P., Kirsch, F., Feldhues, R., Fröbel, T., Nohynek, B., Gabrio, T., 2004. Pathways of trihalomethane uptake in swimming pools. *Int. J. Hyg. Environ. Health* 207 (6), 571–575.

- Fabris, R., Chow, C.W.K., Drikas, M., Eikebrokk, B., 2008. Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Res.* 42 (15), 4188–4196.
- FAC, 2009. Public Swimming Pools and Bathing Places (Chapter 64E-9). Florida Administrative Code & Florida Administrative Register. <https://www.flrules.org/gateway/ChapterHome.asp?Chapter=64e-9>.
- Fan, L., Harris, J.L., Roddick, F.A., Booker, N.A., 2001. Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. *Water Res.* 35 (18), 4455–4463.
- Fang, J.-Y., Ling, L., Shang, C., 2013. Kinetics and mechanisms of pH-dependent degradation of halonitromethanes by UV photolysis. *Water Res.* 47 (3), 1257–1266.
- Fantuzzi, G., Righi, E., Predieri, G., Ceppelli, G., Gobba, F., Aggazzotti, G., 2001. Occupational exposure to trihalomethanes in indoor swimming pools. *Sci. Total Environ.* 264 (3), 257–265.
- Fantuzzi, G., Righi, E., Predieri, G., Giacobazzi, P., Mastroianni, K., Aggazzotti, G., 2010. Prevalence of ocular, respiratory and cutaneous symptoms in indoor swimming pool workers and exposure to disinfection by-products (DBPs). *Int. J. Environ. Res. Public Health* 7 (4), 1379–1391.
- Fischer, K., Fries, E., Körner, W., Schmalz, C., Zwiener, C., 2012. New developments in the trace analysis of organic water pollutants. *Appl. Microbiol. Biotechnol.* 94 (1), 11–28.
- Florentin, A., Hautemanière, A., Hartemann, P., 2011. Health effects of disinfection by-products in chlorinated swimming pools. *Int. J. Hyg. Environ. Health* 214 (6), 461–469.
- Font-Ribera, L., Kogevinas, M., Zock, J.P., Nieuwenhuijsen, M.J., Heederik, D., Villanueva, C.M., 2009. Swimming pool attendance and risk of asthma and allergic symptoms in children. *Eur. Respir. J.* 34 (6), 1304–1310.
- Font-Ribera, L., Kogevinas, M., Schmalz, C., Zwiener, C., Marco, E., Grimalt, J.O., Liu, J., Zhang, X., Mitch, W., Critelli, R., 2016. Environmental and personal determinants of the uptake of disinfection by-products during swimming. *Environ. Res.* 149, 206–215.
- Fujioka, T., Khan, S.J., Poussade, Y., Drewes, J.E., Nghiem, L.D., 2012. N-nitrosamine removal by reverse osmosis for indirect potable water reuse – a critical review based on observations from laboratory-, pilot- and full-scale studies. *Sep. Purif. Technol.* 98, 503–515.
- GB, 1996. Hygienic Standard for Swimming Place. China (GB 9667–1996).
- Glauner, T., Kunz, F., Zwiener, C., Frimmel, F.H., 2005a. Elimination of swimming pool water disinfection by-products with advanced oxidation processes (AOPs). *Acta Hydrochim. Hydrobiol.* 33 (6), 585–594.
- Glauner, T., Waldmann, P., Frimmel, F.H., Zwiener, C., 2005b. Swimming pool water—fractionation and genotoxicological characterization of organic constituents. *Water Res.* 39 (18), 4494–4502.
- Goodman, M., Hays, S., 2008. Asthma and swimming: a meta-analysis. *J. Asthma* 45 (8), 639–647.
- Greyschok, A.E., Vikesland, P.J., 2006. Triclosan reactivity in chloraminated waters. *Environ. Sci. Technol.* 40 (8), 2615–2622.
- Hamidin, N., Yu, Q.J., Connell, D.W., 2008. Human health risk assessment of chlorinated disinfection by-products in drinking water using a probabilistic approach. *Water Res.* 42 (13), 3263–3274.
- Hansen, K.M., Willach, S., Antoniou, M.G., Mosbaek, H., Albrechtsen, H.J., Andersen, H.R., 2012a. Effect of pH on the formation of disinfection byproducts in swimming pool water—is less THM better? *Water Res.* 46 (19), 6399–6409.
- Hansen, K.M., Willach, S., Mosbaek, H., Andersen, H.R., 2012b. Particles in swimming pool filters—does pH determine the DBP formation? *Chemosphere* 87 (3), 241–247.
- Hansen, K.M., Albrechtsen, H.-J., Andersen, H.R., 2013. Optimal pH in chlorinated swimming pools—balancing formation of by-products. *J. Water Health* 11 (3), 465–472.
- Hozalski, R.M., Zhang, L., Arnold, W.A., 2001. Reduction of haloacetic acids by Fe-0: implications for treatment and fate. *Environ. Sci. Technol.* 35 (11), 2258–2263.
- IARC, 1999. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Some Chemicals that Cause Tumours of the Kidney or Urinary Bladder in Rodents and Some Other Substances. vol. 73 World Health Organization. International Agency for Research on Cancer.
- IARC, 2004. IARC monographs on the evaluation of carcinogenic risks to humans. In: Some Drinking-water Disinfectants and Contaminants, Including Arsenic. vol. 84 World Health Organization. International Agency for Research on Cancer.
- IARC, 2014. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Trichloroethylene, Tetrachloroethylene, and Some Other Chlorinated Agents. vol. 106 World Health Organization. International Agency for Research on Cancer.
- Jo, C.H., Dietrich, A.M., Tanko, J.M., 2011. Simultaneous degradation of disinfection byproducts and earthy-musty odors by the UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process. *Water Res.* 45 (8), 2507–2516.
- Jones, C.E., Carpenter, L.J., 2005. Solar photolysis of CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>ClI, and CH<sub>2</sub>IBr in water, saltwater, and seawater. *Environ. Sci. Technol.* 39 (16), 6130–6137.
- Judd, S.J., Black, S.H., 2000. Disinfection by-product formation in swimming pool waters: a simple mass balance. *Water Res.* 34 (5), 1611–1619.
- Judd, S.J., Bullock, G., 2003. The fate of chlorine and organic materials in swimming pools. *Chemosphere* 51 (9), 869–879.
- Kanan, A., 2010. Occurrence and Formation of Disinfection by-Products in Indoor Swimming Pools Water. (PhD thesis).
- Kanan, A., Karanfil, T., 2011. Formation of disinfection by-products in indoor swimming pool water: the contribution from filling water natural organic matter and swimmer body fluids. *Water Res.* 45 (2), 926–932.
- Kanan, A., Selbes, M., Karanfil, T., 2015. In: Karanfil, T., Mitch, B., Westerhoff, P., Xie, Y. (Eds.), Recent Advances in Disinfection by-Products. Amer Chemical Soc, Washington, pp. 405–430.
- Keuten, M.G., Schets, F.M., Schijven, J.F., Verberk, J.Q., van Dijk, J.C., 2012. Definition and quantification of initial anthropogenic pollutant release in swimming pools. *Water Res.* 46 (11), 3682–3692.
- Keuten, M.G.A., Peters, M.C.F.M., Daanen, H.A.M., de Kreuk, M.K., Rietveld, L.C., van Dijk, J.C., 2014. Quantification of continual anthropogenic pollutants released in swimming pools. *Water Res.* 53, 259–270.
- Kim, H., Halmteier, P., Klotz, J.B., Weisel, C.P., 1999. Evaluation of biomarkers of environmental exposures: urinary haloacetic acids associated with ingestion of chlorinated drinking water. *Environ. Res.* 80 (2), 187–195.
- Kim, H., Shim, J., Lee, S., 2002. Formation of disinfection by-products in chlorinated swimming pool water. *Chemosphere* 46 (1), 123–130.
- Kimura, K., Amy, G., Drewes, J.E., Heberer, T., Kim, T.-U., Watanabe, Y., 2003. Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. *J. Membr. Sci.* 227 (1), 113–121.
- Klüpfel, A.M., Glauner, T., Zwiener, C., Frimmel, F.H., 2011. Nanofiltration for enhanced removal of disinfection by-product (DBP) precursors in swimming pool water—retention and water quality estimation. *Water Sci. Technol.* 63 (8), 1716–1725.
- Kogevinas, M., Villanueva, C., Font Ribera, L., Liviác, D., Bustamante, M., Espinoza, F., Nieuwenhuijsen, M., Espinosa, A., Fernandez, P., DeMarini, D., Grimalt, J., Grummt, T., Marcos, R., 2010. Genotoxic effects in swimmers exposed to disinfection by-products in indoor swimming pools. *Environ. Health Perspect.* 118 (11), 1531–1537.
- Kong, F.-x., Yang, H.-w., Wang, X.-m., Xie, Y.F., 2014. Rejection of nine haloacetic acids and coupled reverse draw solute permeation in forward osmosis. *Desalination* 341 (1–9).
- Korshin, G.V., Jensen, M.D., 2001. Electrochemical reduction of haloacetic acids and exploration of their removal by electrochemical treatment. *Electrochim. Acta* 47 (5), 747–751.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Sclementi, M.J., Onstad, G.D., Thruston, A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40 (23), 7175–7185.
- Kwok, W.M., Zhao, C., Li, Y.-L., Guan, X., Wang, D., Phillips, D.L., 2004. Water-catalyzed dehalogenation reactions of isobromoforn and its reaction products. *J. Am. Chem. Soc.* 126 (10), 3119–3131.
- Lambropoulou, D.A., Giokas, D.L., Sakkas, V.A., Albanis, T.A., Karayannis, M.I., 2002. Gas chromatographic determination of 2-hydroxy-4-methoxybenzophenone and octyldimethyl-p-aminobenzoic acid sunscreen agents in swimming pool and bathing waters by solid-phase microextraction. *J. Chromatogr. A* 967 (2), 243–253.
- Lamont Bradford, W., 2014. What bathers put into a pool: a critical review of body fluids and a body fluid analog. *Int. J. Aquat. Res. Educ.* 8 (2), 168–181.
- Lee, J., Ha, K.T., Zoh, K.D., 2009. Characteristics of trihalomethane (THM) production and associated health risk assessment in swimming pool waters treated with different disinfection methods. *Sci. Total Environ.* 407 (6), 1990–1997.
- Lee, J., Jun, M.J., Lee, M.H., Eom, S.W., Zoh, K.D., 2010. Production of various disinfection byproducts in indoor swimming pool waters treated with different disinfection methods. *Int. J. Hyg. Environ. Health* 213 (6), 465–474.
- Lévesque, B., Ayotte, P., Tardif, R., Charest-Tardif, G., 2000. Evaluation of the health risk associated with exposure to chloroform in indoor swimming pools. *J. Toxicol. Environ. Health* A 61 (4), 225–243.
- Li, J., Blatchley, E.R., 2007. Volatile disinfection byproduct formation resulting from chlorination of organic-nitrogen precursors in swimming pools. *Environ. Sci. Technol.* 41 (19), 6732–6739.
- Lian, L., Li, J., Blatchley III, E.R., 2014. Volatile disinfection byproducts resulting from chlorination of uric acid: implications for swimming pools. *Environ. Sci. Technol.* 48 (6), 3210–3217.
- Lifongo, L.L., Bowden, D.J., Brimblecombe, P., 2004. Photodegradation of haloacetic acids in water. *Chemosphere* 55 (3), 467–476.
- Lifongo, L.L., Bowden, D.J., Brimblecombe, P., 2010. Thermal degradation of haloacetic acids in water. *Int. J. Phys. Sci.* 5 (6), 738–747.
- Liu, W., Cheung, L.-M., Yang, X., Shang, C., 2006. THM, HAA and CNCl formation from UV irradiation and chlor(am)ination of selected organic waters. *Water Res.* 40 (10), 2033–2043.
- Liviác, D., Wagner, E.D., Mitch, W.A., Altonji, M.J., Plewa, M.J., 2010. Genotoxicity of water concentrates from recreational pools after various disinfection methods. *Environ. Sci. Technol.* 44 (9), 3527–3532.
- Loos, R., Barceló, D., 2001. Determination of haloacetic acids in aqueous environments by solid-phase extraction followed by ion-pair liquid chromatography–electrospray ionization mass spectrometric detection. *J. Chromatogr. A* 938 (1–2), 45–55.
- Lourencetti, C., Grimalt, J.O., Marco, E., Fernandez, P., Font-Ribera, L., Villanueva, C.M., Kogevinas, M., 2012. Trihalomethanes in chlorine and bromine disinfected swimming pools: air-water distributions and human exposure. *Environ. Int.* 45, 59–67.
- Manasfi, T., Storck, V., Ravier, S., Demelas, C., Coulomb, B., Boudenne, J.L., 2015. Degradation products of benzophenone-3 in chlorinated seawater swimming pools. *Environ. Sci. Technol.* 49 (15), 9308–9316.
- Manasfi, T., De Méo, M., Coulomb, B., Di Giorgio, C., Boudenne, J.-L., 2016. Identification of disinfection by-products in freshwater and seawater swimming pools and evaluation of genotoxicity. *Environ. Int.* 88, 94–102.
- Manasfi, T., Coulomb, B., Boudenne, J.L., 2017a. Occurrence, origin, and toxicity of disinfection byproducts in chlorinated swimming pools: an overview. *Int. J. Hyg. Environ. Health* 220 (3), 591–603.
- Manasfi, T., Coulomb, B., Ravier, S., Boudenne, J.L., 2017b. Degradation of organic UV filters in chlorinated seawater swimming pools: transformation pathways and bromoform formation. *Environ. Sci. Technol.* 51 (23), 13580–13591.
- Manasfi, T., De Meo, M., Di Giorgio, C., Coulomb, B., Boudenne, J.L., 2017c. Assessing the genotoxicity of two commonly occurring byproducts of water disinfection: chloral hydrate and bromal hydrate. *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* 813, 37–44.
- Marina, L.S., Ibarluzea, J., Basterrechea, M., Goñi, F., Ulibarrena, E., Artieda, J., Orruño,



- I., 2009. Indoor air and bathing water pollution in indoor swimming pools in Guipuzcoa (Spain). *Gac. Sanit.* 23 (2), 115–120.
- Massin, N., Bohadana, A.B., Wild, P., Hery, M., Toamain, J.P., Hubert, G., 1998. Respiratory symptoms and bronchial responsiveness in lifeguards exposed to nitrogen trichloride in indoor swimming pools. *Occup. Environ. Med.* 55 (4), 258–263.
- Matilainen, A., Sillanpää, M., 2010. Removal of natural organic matter from drinking water by advanced oxidation processes. *Chemosphere* 80 (4), 351–365.
- Michalski, R., Mathews, B., 2007. Occurrence of chlorite, chlorate and bromate in disinfected swimming pool water. *Pol. J. Environ. Stud.* 16 (2), 237–241.
- Moffa, P.E., Davis, D.P., Somerlot, C., Sharek, D., Gresser, B., Smith, T., 2006. Alternative disinfection technology demonstrates advantages for wet weather applications—a pilot study of powdered bromine technology. *Proc. Water Environ. Fed.* 2006 (12), 1202–1218.
- Muellner, M.G., Wagner, E.D., McCalla, K., Richardson, S.D., Woo, Y.-T., Plewa, M.J., 2007. Haloacetonitriles vs. regulated haloacetic acids: are nitrogen-containing DBPs more toxic? *Environ. Sci. Technol.* 41 (2), 645–651.
- Nakajima, M., Kawakami, T., Niino, T., Takahashi, Y., Onodera, S., 2009. Aquatic fate of sunscreen agents octyl-4-methoxycinnamate and octyl-4-dimethylaminobenzoate in model swimming pools and the mutagenic assays of their chlorination byproducts. *J. Health Sci.* 55 (3), 363–372.
- Nassan, F.L., Coull, B.A., Gaskins, A.J., Williams, M.A., Skakkebaek, N.E., Ford, J.B., Ye, X.Y., Calafat, A.M., Braun, J.M., Hauser, R., 2017. Personal care product use in men and urinary concentrations of select phthalate metabolites and parabens: results from the environment and reproductive health (EARTH) study. *Environ. Health Perspect.* 125 (8).
- NEA, 2005. Code of Practice on Environmental Health. National Environment Agency, Singapore.
- NEA, 2008. Environmental Public Health Act. Chapter 95. In: Environmental Public Health (Quality of Piped Drinking Water) Regulations.
- Negreira, N., Canosa, P., Rodríguez, I., Ramil, M., Rubí, E., Cela, R., 2008. Study of some UV filters stability in chlorinated water and identification of halogenated by-products by gas chromatography-mass spectrometry. *J. Chromatogr. A* 1178 (1–2), 206–214.
- NHMC, 2011. Australian Drinking Water Guidelines 6, National Water Quality Management Strategy. National Health and Medical Research Council, Australian Government.
- Nitter, T.B., Kampel, W., Svendsen, K.V.H., Aas, B., 2018. Comparison of trihalomethanes in the air of two indoor swimming pool facilities using different type of chlorination and different types of water. *Water Sci. Technol.* 18 (4), 1350–1356.
- NSPF, 2006. Certified Pool-Spa Operator Handbook. National Swimming Pool Foundation, Colorado Springs, CO.
- Panyakapo, M., Soontornchai, S., Paopuree, P., 2008. Cancer risk assessment from exposure to trihalomethanes in tap water and swimming pool water. *J. Environ. Sci.* 20 (3), 372–378.
- Pardo, A., Nevo, K., Vigiser, D., Lazarov, A., 2007. The effect of physical and chemical properties of swimming pool water and its close environment on the development of contact dermatitis in hydrotherapists. *Am. J. Ind. Med.* 50 (2), 122–126.
- Parinet, J., Tabaries, S., Coulomb, B., Vassallo, L., Boudenne, J.L., 2012. Exposure levels to brominated compounds in seawater swimming pools treated with chlorine. *Water Res.* 46 (3), 828–836.
- Pereira, I., Sá, C.S.A., Boaventura, R.A.R., 2012. Analysis of haloacetic acids in water and air (aerosols) from indoor swimming pools using HS-SPME/GC/ECD. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 47 (2), 176–183.
- Plewa, M.J., Wagner, E.D., Muellner, M.G., Hsu, K.-M., Richardson, S.D., 2008. Disinfection by-Products in Drinking Water. American Chemical Society, pp. 36–50.
- Pluchon, C., Serodes, J.B., Berthiaume, C., Charette, S.J., Gilbert, Y., Filion, G., Fournier-Larente, J., Rodriguez, M., Duchaine, C., 2013. Haloacetic acid degradation by a biofilm in a simulated drinking water distribution system. *Water Sci. Technol. Water Supply* 13 (2), 447–461.
- Queensland, G., 2004. Queensland Health Swimming and Spa Pool Water Quality and Operational Guidelines. pp. 10.
- Rahman, M.B., Driscoll, T., Cowie, C., Armstrong, B.K., 2010. Disinfection by-products in drinking water and colorectal cancer: a meta-analysis. *Int. J. Epidemiol.* 39 (3), 733–745.
- Richardson, S.D., Thruston, A.D., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, B.W., Sun, G.-r., Majetich, G., 1999. Identification of new ozone disinfection byproducts in drinking water. *Environ. Sci. Technol.* 33 (19), 3368–3377.
- Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., Demarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat. Res.* 636 (1–3), 178–242.
- Richardson, S.D., DeMarini, D.M., Kogevinas, M., Fernandez, P., Marco, E., Lourencetti, C., Ballesté, C., Heederik, D., Meliefste, K., McKague, A.B., 2010. What's in the pool? A comprehensive identification of disinfection by-products and assessment of mutagenicity of chlorinated and brominated swimming pool water. *Environ. Health Perspect.* 118 (11), 1523–1530.
- Rook, J.J., 1974. Formation of haloforms during chlorination of natural water. *Water Treat. Examination* 23, 234–243.
- Rudra, A., Thacker, N., Pande, S., 2005. Hydrogen peroxide and ultraviolet irradiations in water treatment. *Environ. Monit. Assess.* 109 (1–3), 189–197.
- Rule, K.L., Ebbett, V.R., Vikesland, P.J., 2005. Formation of chloroform and chlorinated organics by free-chlorine-mediated oxidation of triclosan. *Environ. Sci. Technol.* 39 (9), 3176–3185.
- Sadiq, R., Rodriguez, M.J., 2004. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. *Sci. Total Environ.* 321 (1–3), 21–46.
- Sakkas, V.A., Giokas, D.L., Lambropoulou, D.A., Albanis, T.A., 2003. Aqueous photolysis of the sunscreen agent octyl-dimethyl-p-aminobenzoic acid: formation of disinfection byproducts in chlorinated swimming pool water. *J. Chromatogr. A* 1016 (2), 211–222.
- Sarrión, M.N., Santos, F.J., Galceran, M.T., 2000. In situ derivatization/solid-phase microextraction for the determination of haloacetic acids in water. *Anal. Chem.* 72 (20), 4865–4873.
- Schmalz, C., 2012. Formation, Phase Transfer and Toxicity of Halogenated Disinfection by-Products in the Processing Cycle of Swimming Pool Water. (PhD thesis).
- Schmalz, C., Frimmel, F.H., Zwiener, C., 2011. Trichloramine in swimming pools—formation and mass transfer. *Water Res.* 45 (8), 2681–2690.
- Sentana, I., Rodriguez, M., Sentana, E., Prats, D., 2010. Effect of pressure and pH over the removal of disinfection by-products using nanofiltration membranes in discontinuous systems. *Desalination Water Treat.* 23 (1–3), 3–12.
- Serpone, N., Salinaro, A., Emeline, A.V., Horikoshi, S., Hidaka, H., Zhao, J., 2002. An in vitro systematic spectroscopic examination of the photostabilities of a random set of commercial sunscreen lotions and their chemical UVB/UVA active agents. *Photochem. Photobiol. Sci.* 1 (12), 970–981.
- Sharpless, C.M., Linden, K.G., 2003. Experimental and model comparisons of low- and medium-pressure hg lamps for the direct and H<sub>2</sub>O<sub>2</sub> assisted UV photodegradation of N-nitrosodimethylamine in simulated drinking water. *Environ. Sci. Technol.* 37 (9), 1933–1940.
- Shen, R., Andrews, S.A., 2011. Demonstration of 20 pharmaceuticals and personal care products (PPCPs) as nitrosamine precursors during chloramine disinfection. *Water Res.* 45 (2), 944–952.
- Simard, S., Tardif, R., Rodriguez, M.J., 2013. Variability of chlorination by-product occurrence in water of indoor and outdoor swimming pools. *Water Res.* 47 (5), 1763–1772.
- Soltermann, F., Lee, M., Canonica, S., von Gunten, U., 2013. Enhanced N-nitrosamine formation in pool water by UV irradiation of chlorinated secondary amines in the presence of monochloramine. *Water Res.* 47 (1), 79–90.
- Spain, 2007. Swimming Pool Regulations. <https://www.eyenospain.com/spain-magazine/pool-legals.aspx>.
- Spangenberg, D., Möller, U., Kleinermanns, K., 1996. Photooxidation of exhaust pollutants IV. Photocatalytic and thermal decomposition of trichloroacetic acid: degradation efficiencies and products. *Chemosphere* 33 (1), 43–49.
- Stack, M.A., Fitzgerald, G., O'Connell, S., James, K.J., 2000. Measurement of trihalomethanes in potable and recreational waters using solid phase micro extraction with gas chromatography-mass spectrometry. *Chemosphere* 41 (11), 1821–1826.
- Stottmeister, E., Naglitsch, F., 1996. Human Exposure to Other Disinfection by-Products than Trihalomethanes in Swimming Pools. Annual Report of the Federal Environmental Agency, Berlin, Germany. (in German).
- Suppes, L.M., Huang, C.H., Lee, W.N., Brockman, K.J., 2017. Sources of pharmaceuticals and personal care products in swimming pools. *J. Water Health* 15 (5), 829–833.
- Tang, S., Wang, X.M., Yang, H.W., Xie, Y.F.F., 2013. Haloacetic acid removal by sequential zero-valent iron reduction and biologically active carbon degradation. *Chemosphere* 90 (4), 1563–1567.
- Teo, T.L.L., Coleman, H.M., Khan, S.J., 2015. Chemical contaminants in swimming pools: occurrence, implications and control. *Environ. Int.* 76, 16–31.
- Teo, T.L.L., Coleman, H.M., Khan, S.J., 2016. Occurrence and daily variability of pharmaceuticals and personal care products in swimming pools. *Environ. Sci. Pollut. Res.* 23 (7), 6972–6981.
- Terasaki, M., Makino, M., 2008. Determination of chlorinated by-products of parabens in swimming pool water. *Int. J. Environ. Anal. Chem.* 88 (13), 911–922.
- Tung, H.H., Xie, Y.F., 2009. Association between haloacetic acid degradation and heterotrophic bacteria in water distribution systems. *Water Res.* 43 (4), 971–978.
- Uyak, V., Koyuncu, I., Oktem, I., Cakmakci, M., Toroz, I., 2008. Removal of trihalomethanes from drinking water by nanofiltration membranes. *J. Hazard. Mater.* 152 (2), 789–794.
- Vidal, L., Chisvert, A., Canals, A., Salvador, A., 2010. Ionic liquid-based single-drop microextraction followed by liquid chromatography-ultraviolet spectrophotometry detection to determine typical UV filters in surface water samples. *Talanta* 81 (1–2), 549–555.
- Villanueva, C., Font Ribera, L., 2012. Health impact of disinfection by-products in swimming pools. *Ann. Ist. Super. Sanita* 48 (4), 387–396.
- Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Castaño-Vinyals, G., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., 2006. Assessment of lifetime exposure to trihalomethanes through different routes. *Occup. Environ. Med.* 63 (4), 273–277.
- Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castano-Vinyals, G., 2007a. Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools. *Am. J. Epidemiol.* 165 (2), 148–156.
- Villanueva, C.M., Gagniere, B., Monfort, C., Nieuwenhuijsen, M.J., Cordier, S., 2007b. Sources of variability in levels and exposure to trihalomethanes. *Environ. Res.* 103 (2), 211–220.
- Von Gunten, U., Oliveras, Y., 1998. Advanced oxidation of bromide-containing waters: bromate formation mechanisms. *Environ. Sci. Technol.* 32 (1), 63–70.
- Walse, S.S., Mitch, W.A., 2008. Nitrosamine carcinogens also swim in chlorinated pools. *Environ. Sci. Technol.* 42 (4), 1032–1037.
- Wang, G.-S., Hsieh, S.-T., Hong, C.-S., 2000. Destruction of humic acid in water by UV light—catalyzed oxidation with hydrogen peroxide. *Water Res.* 34 (15), 3882–3887.
- Wang, W., Qian, Y., Boyd, J.M., Wu, M., Hrudey, S.E., Li, X.F., 2013. Halobenzoquinones in swimming pool waters and their formation from personal care products. *Environ. Sci. Technol.* 47 (7), 3275–3282.
- Wang, X., Leal, M.G., Zhang, X., Yang, H., Xie, Y., 2014. Haloacetic acids in swimming

- pool and spa water in the United States and China. *Front. Environ. Sci. Eng.* 1–5.
- Weaver, W.A., Li, J., Wen, Y., Johnston, J., Blatchley, M.R., Blatchley III, E.R., 2009. Volatile disinfection by-product analysis from chlorinated indoor swimming pools. *Water Res.* 43 (13), 3308–3318.
- Weng, S., Blatchley III, E.R., 2011. Disinfection by-product dynamics in a chlorinated, indoor swimming pool under conditions of heavy use: national swimming competition. *Water Res.* 45 (16), 5241–5248.
- Weng, S., Li, J., Blatchley III, E.R., 2012. Effects of UV254 irradiation on residual chlorine and DBPs in chlorination of model organic-N precursors in swimming pools. *Water Res.* 46 (8), 2674–2682.
- Weng, S.C., Li, J., Wood, K.V., Kenttamaa, H.I., Williams, P.E., Amundson, L.M., Blatchley, E.R., 2013. UV-induced effects on chlorination of creatinine. *Water Res.* 47 (14), 4948–4956.
- Weng, S., Sun, P., Ben, W., Huang, C.-H., Lee, L.T., Blatchley III, E.R., 2014. The presence of pharmaceuticals and personal care products in swimming pools. *Environ. Sci. Technol. Lett.* 1 (12), 495–498.
- White, G., 1999. *Handbook of Chlorination and Alternative Disinfectants*, 1999. John Wiley and Sons, New York.
- WHO, 2006. *Guidelines for Safe Recreational Water Environments. Swimming Pools and Similar Environments*, vol. 2.
- WHO, 2008. *Guidelines for Drinking-water Quality*, Third edition. Recommendations, vol. 1.
- WHO, 2018. *Bromine as a Drinking-water Disinfectant*.
- Wiant, C., 2011. A snapshot of swimmer hygiene behavior. *Int. J. Aquat. Res. Educ.* 5 (3), 3.
- Wojtowicz, J.A., 1996. Relative bactericidal effectiveness of hypochlorous acid and chloroisocyanurates. *J. Swim. Pool Spa Ind.* 2 (1), 34–41.
- Wojtowicz, J.A., 2004. Effect of cyanuric acid on swimming pool maintenance. *J. Swim. Pool Spa Ind.* 5 (1), 15–19.
- Wu, C., Wei, D., Fan, J., Wang, L., 2001. Photosonochemical degradation of tri-chloroacetic acid in aqueous solution. *Chemosphere* 44 (5), 1293–1297.
- Xiao, F., Zhang, X., Zhai, H., Lo, I.M., Tipoe, G.L., Yang, M., Pan, Y., Chen, G., 2012. New halogenated disinfection byproducts in swimming pool water and their permeability across skin. *Environ. Sci. Technol.* 46 (13), 7112–7119.
- Xiao, Y., Fan, R., Zhang, L., Yue, J., Webster, R.D., Lim, T.-T., 2014. Photodegradation of iodinated trihalomethanes in aqueous solution by UV 254 irradiation. *Water Res.* 49, 275–285.
- Xu, X., Mariano, T.M., Laskin, J.D., Weisel, C.P., 2002. Percutaneous absorption of tri-halomethanes, haloacetic acids, and haloketones. *Toxicol. Appl. Pharmacol.* 184 (1), 19–26.
- Xu, P., Drewes, J.E., Bellona, C., Amy, G., Kim, T.-U., Adam, M., Heberer, T., 2005. Rejection of emerging organic micropollutants in nanofiltration–reverse osmosis membrane applications. *Water Environ. Res.* 77 (1), 40–48.
- Xu, B., Chen, Z., Qi, F., Ma, J., Wu, F., 2009. Rapid degradation of new disinfection by-products in drinking water by UV irradiation: *N*-nitrosopyrrolidine and *N*-nitrosopiperidine. *Sep. Purif. Technol.* 69 (1), 126–133.
- Yang, L., Schmalz, C., Zhou, J., Zwiener, C., Chang, V.W.C., Ge, L., Wan, M.P., 2016. An insight of disinfection by-product (DBP) formation by alternative disinfectants for swimming pool disinfection under tropical conditions. *Water Res.* 101, 535–546.
- Yang, L., She, Q., Wan, M.P., Wang, R., Chang, V.W.C., Tang, C.Y., 2017a. Removal of haloacetic acids from swimming pool water by reverse osmosis and nanofiltration. *Water Res.* 116, 116–125.
- Yang, L., Zhou, J., She, Q., Wan, M.P., Wang, R., Chang, V.W.C., Tang, C.Y., 2017b. Role of calcium ions on the removal of haloacetic acids from swimming pool water by nanofiltration: mechanisms and implications. *Water Res.* 110, 332–341.
- Yeh, R.Y.L., Farré, M.J., Stalter, D., Tang, J.Y.M., Molendijk, J., Escher, B.I., 2014. Bioanalytical and chemical evaluation of disinfection by-products in swimming pool water. *Water Res.* 59, 172–184.
- Zhang, X., Minear, R.A., 2002. Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water. *Water Res.* 36 (14), 3665–3673.
- Zwiener, C., Richardson, S.D., De Marini, D.M., Grummt, T., Glauner, T., Frimmel, F.H., 2007. Drowning in disinfection byproducts? Assessing swimming pool water. *Environ. Sci. Technol.* 41 (2), 363–372.